Support Information

Visible Light-Mediated Deoxygenation Protocol for Synthesis of Dipeptide, Amide and Ester without Racemization

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Table of Contents

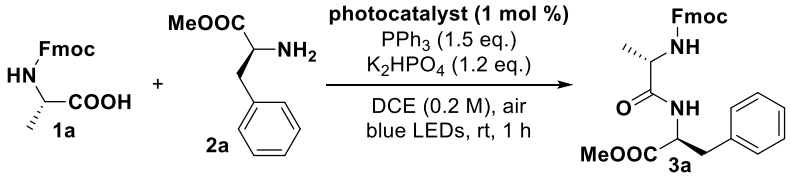
1. General experimental information

Unless otherwise noted, all the substrates and reagents were purchased from commercial suppliers and used without further purification, which were known compounds. ^{1}H NMR spectra were recorded at 500 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 125 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. High resolution mass spectroscopy (HRMS) was performed on Thermo Q Exactive Plus (FTMS ESI) mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh).

2. Experimental procedures and characterization data

2.1. Optimization studies

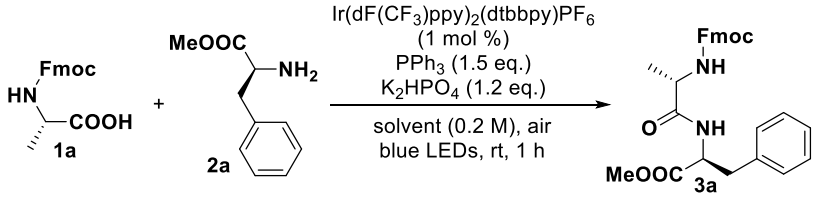
Table S1. The effects of photocatalyst[a]



Entry	Photocatalyst	Yield (%)[b]
1	$Ru(bpy)_3(PF_6)_2$	trace
2	$Ru(bpz)_3(PF_6)_2$	trace
3	$Ir(ppy)_2(dtbbpy)PF_6$	trace
4	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	58
5	**$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$**	**87**
6	*fac*-$Ir(ppy)_3$	trace
7	Rose Bengal	trace
8	Eosin Y	trace
9	Rhodamine B	trace
10	DCA	trace

[a]Unless otherwise noted, all reactions were carried out using amino acid **1a** (0.2 mmol, 1.0 equiv.), amino acid ester **2a** (0.24 mmol, 1.2 equiv.), photocatalyst (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and K_2HPO_4 (0.24 mmol, 1.2 equiv.) in 1,2-dichloroethane (1.0 mL) at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). [b]Isolated yield with >20:1 *dr* determined by ^1H NMR.

Table S2. The effects of solvent[a]

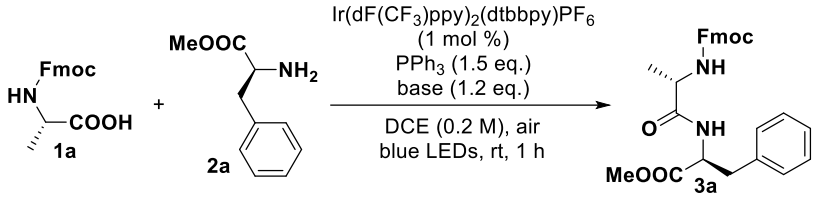


Entry	Solvent	Yield (%)[b]
1	**DCE**	**87**
2	MeCN	47
3	DMF	68
4	EtOH	NR

5	THF	40
6	toluene	trace
7	1,4-dioxane	trace

[a]Unless otherwise noted, all reactions were carried out using amino acid **1a** (0.2 mmol, 1.0 equiv.), amino acid ester **2a** (0.24 mmol, 1.2 equiv.), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and K_2HPO_4 (0.24 mmol, 1.2 equiv.) in solvent (1.0 mL) at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). [b]Isolated yield with >20:1 *dr* determined by ^1H NMR.

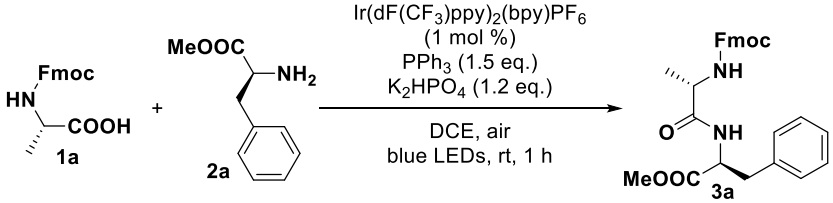
Table S3. The effects of base[a]



Entry	Base	Yield (%)[b]
1	**K_2HPO_4**	**87**
2	-	50
3	$NaHCO_3$	39
4	Na_2CO_3	41
5	K_2CO_3	51

[a]Unless otherwise noted, all reactions were carried out using amino acid **1a** (0.2 mmol, 1.0 equiv.), amino acid ester **2a** (0.24 mmol, 1.2 equiv.), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and base (0.24 mmol, 1.2 equiv.) in 1,2-dichloroethane (1.0 mL) at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). [b]Isolated yield with >20:1 *dr* determined by ^1H NMR.

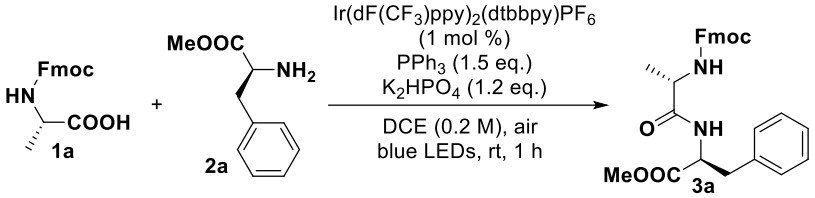
Table S4. The effects of concentration[a]



Entry	Concentration	Yield (%)[b]
1	0.1	76
2	0.5	85

[a]Unless otherwise noted, all reactions were carried out using amino acid **1a** (0.2 mmol, 1.0 equiv.), amino acid ester **2a** (0.24 mmol, 1.2 equiv.), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and K_2HPO_4 (0.24 mmol, 1.2 equiv.) in 1,2-dichloroethane at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). [b]Isolated yield with >20:1 *dr* determined by ^1H NMR.

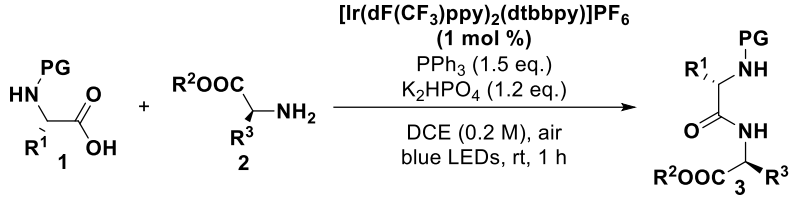
Table S5. Control experiments[a]



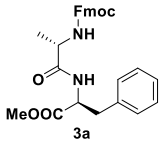
Entry	Variation from the standard conditions	Yield (%)[b]
1	5 mol % of $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	88
2	no photocatalyst	NR
3	in dark	NR
4	no PPh_3	NR

[a]Unless otherwise noted, all reactions were carried out using amino acid **1a** (0.2 mmol, 1.0 equiv.), amino acid ester **2a** (0.24 mmol, 1.2 equiv.), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and K_2HPO_4 (0.24 mmol, 1.2 equiv.) in 1,2-dichloroethane (1.0 mL) at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). [b]Isolated yield with >20:1 *dr* determined by ^1H NMR.

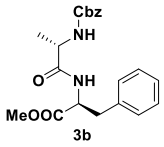
2.2. General procedure for the synthesis of dipeptides 3



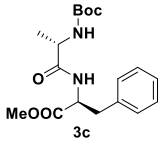
N-protected amino acids **1** (0.2 mmol, 1.0 equiv.), amino acid esters **2** (0.24 mmol, 1.2 equiv.), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and K_2HPO_4 (0.24 mmol, 1.2 equiv.) were well mixed in 1,2-dichloroethane (1.0 mL). The resulting mixture was stirred at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (EtOAc/PE = 20%-40%) to yield dipeptides **3**.



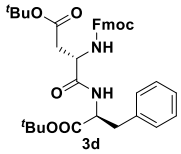
Dipeptide 3a[1]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (82.4 mg, 87% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.31 (td, J = 7.5, 0.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 2H), 7.17-7.20 (m, 1H), 7.07 (d, J = 7.5 Hz, 2H), 6.42 (d, J = 6.5 Hz, 1H), 5.30 (d, J = 6.0 Hz, 1H), 4.84-4.88 (m, 1H), 4.38-4.42 (m, 1H), 4.32-4.36 (m, 1H), 4.19-4.24 (m, 2H), 3.72 (s, 3H), 3.15 (dd, J = 14.0, 5.5 Hz, 1H), 3.07 (dd, J = 14.0, 6.5 Hz, 1H), 1.35 (d, J = 6.5 Hz, 3H).



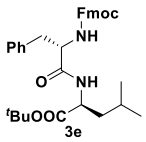
Dipeptide 3b[2]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (62.1 mg, 81% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.38 (m, 5H), 7.21-7.28 (m, 3H), 7.08 (d, J = 7.0 Hz, 2H), 6.44 (d, J = 4.5 Hz, 1H), 5.23 (d, J = 4.5 Hz, 1H), 5.06-5.13 (m, 2H), 4.83-4.87 (m, 1H), 4.20-4.23 (m, 1H), 3.72 (s, 3H), 3.15 (dd, J = 14.0, 6.0 Hz, 1H), 3.07 (dd, J = 14.0, 6.0 Hz, 1H), 1.33 (d, J = 7.0 Hz, 3H).



Dipeptide 3c[3]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (55.4 mg, 79% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.30 (m, 3H), 7.09-7.11 (m, 2H), 6.52 (d, J = 7.5 Hz, 1H), 4.93 (*br* s, 1H), 4.83-4.87 (m, 1H), 4.14 (*br* s, 1H), 3.71 (s, 3H), 3.16 (dd, J = 14.0, 6.0 Hz, 1H), 3.10 (dd, J = 14.0, 6.0 Hz, 1H), 1.44 (s, 9H), 1.31 (d, J = 7.0 Hz, 3H).

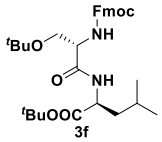


Dipeptide 3d[4]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (109.8 mg, 89% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.29-7.32 (m, 2H), 7.24-7.27 (m, 2H), 7.18-7.21 (m, 3H), 7.02 (d, J = 7.0 Hz, 1H), 5.95 (d, J = 8.0 Hz, 1H), 4.66-4.70 (m, 1H), 4.54 (d, J = 3.0 Hz, 1H), 4.32-4.41 (m, 2H), 4.21 (t, J = 7.0 Hz, 1H), 3.08 (d, J = 6.0 Hz, 2H), 2.90 (dd, J = 17.0, 4.0 Hz, 1H), 2.62 (dd, J = 17.0, 6.5 Hz, 1H), 1.44 (s, 9H), 1.37 (s, 9H).

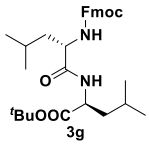


Dipeptide 3e[4]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (100.2 mg, 90% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz,

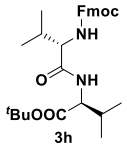
2H), 7.54 (t, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.21-7.24 (m, 1H), 7.18 (d, *J* = 5.0 Hz, 2H), 6.15 (d, *J* = 6.5 Hz, 1H), 5.33 (d, *J* = 6.5 Hz, 1H), 4.42-4.46 (m, 3H), 4.30-4.33 (m, 1H), 4.19 (t, *J* = 6.5 Hz, 1H), 3.03-3.14 (m, 2H), 1.52-1.56 (m, 2H), 1.42-1.46 (m, 10H), 0.90 (d, *J* = 6.0 Hz, 3H), 0.88 (d, *J* = 6.0 Hz, 3H).



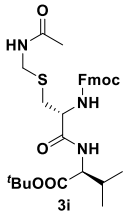
Dipeptide 3f[4]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (88.4 mg, 80% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.59-7.62 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.30-7.33 (m, 2H), 7.22 (d, *J* = 6.5 Hz, 1H), 5.78 (d, *J* = 4.5 Hz, 1H), 4.47-4.48 (m, 1H), 4.37-4.43 (m, 2H), 4.22-4.25 (m, 2H), 3.83 (dd, *J* = 8.5, 3.5 Hz, 1H), 3.40 (t, *J* = 8.5 Hz, 1H), 1.67-1.71 (m, 1H), 1.60-1.65 (m, 1H), 1.50-1.55 (m, 1H), 1.46 (s, 9H), 1.23 (s, 9H), 0.95 (d, *J* = 6.5 Hz, 6H).



Dipeptide 3g[4]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (88.9 mg, 85% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (tt, *J* = 7.5, 1.0 Hz, 2H), 6.28 (d, *J* = 8.0 Hz, 1H), 5.26 (d, *J* = 8.0 Hz, 1H), 4.45-4.50 (m, 1H), 4.35-4.43 (m, 2H), 4.21 (t, *J* = 7.0 Hz, 2H), 1.50-1.67 (m, 6H), 1.45 (s, 9H), 0.95 (d, *J* = 3.0 Hz, 6H), 0.91 (dd, *J* = 6.0, 2.0 Hz, 6H).

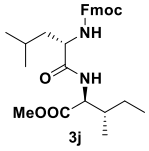


Dipeptide 3h[4]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (81.4 mg, 82% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29-7.32 (m, 2H), 6.28 (d, *J* = 8.5 Hz, 1H), 5.46 (d, *J* = 8.5 Hz, 1H), 4.41-4.44 (m, 2H), 4.35-4.38 (m, 1H), 4.23 (t, *J* = 7.0 Hz, 1H), 4.05 (t, *J* = 7.5 Hz, 1H), 2.11-2.17 (m, 2H), 1.46 (s, 9H), 0.97 (t, *J* = 8.0 Hz, 6H), 0.91 (dd, *J* = 10.0, 7.0 Hz, 6H).

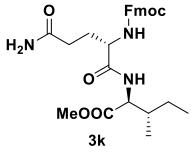


Dipeptide 3i[5]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); Colorless oil (89.8 mg, 79% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.66 (*br* s, 1H), 5.97 (d, *J* = 8.0 Hz, 1H), 4.78 (dd, *J* = 14.0, 7.5 Hz, 1H), 4.68 (dd, *J* = 12.5, 7.5 Hz, 1H), 4.35-4.41 (m, 3H), 4.22-4.26 (m, 2H), 3.01

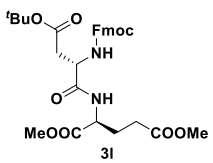
(dd, J = 14.5, 4.5 Hz, 1H), 2.73 (dd, J = 14.5, 8.0 Hz, 1H), 2.18-2.26 (m, 1H), 2.05 (s, 3H), 1.46 (s, 9H), 0.97 (t, J = 7.5 Hz, 6H).



Dipeptide 3j: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (88.4 mg, 92% yield, >20:1 dr); m.p. 120-121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 6.5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.28 (td, J = 7.5, 1.0 Hz, 2H), 6.71 (d, J = 8.5 Hz, 1H), 5.49 (d, J = 8.5 Hz, 1H), 4.58 (dd, J = 8.5, 5.0 Hz, 1H), 4.34-4.42 (m, 2H), 4.29-4.31 (m, 1H), 4.20 (t, J = 7.0 Hz, 1H), 3.70 (s, 3H), 1.88 (*br* s, 1H), 1.63-1.71 (m, 2H), 1.54-1.57 (m, 1H), 1.38-1.42 (m, 1H), 1.13-1.19 (m, 1H), 0.94 (s, 6H), 0.85-0.88 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2(2), 172.1(9), 156.3, 143.9, 143.8, 141.3, 127.8, 127.1, 125.1, 120.0(1), 119.9(9), 67.1, 56.5, 53.5, 52.1, 47.1, 41.5, 37.8, 25.2, 24.7, 22.9, 22.1, 15.4, 11.6; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{36}N_2NaO_5^+$ 503.2516, found 503.2526.

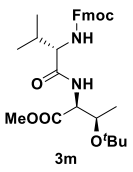


Dipeptide 3k: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (85.9 mg, 87% yield, >20:1 dr); m.p. 210-211 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 7.80 (d, J = 7.5 Hz, 2H), 7.67 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 4.33-4.42 (m, 3H), 4.21-4.26 (m, 2H), 3.72 (s, 3H), 2.35 (t, J = 7.5 Hz, 2H), 2.05-2.12 (m, 1H), 1.88-1.96 (m, 2H), 1.45-1.51 (m, 1H), 1.22-1.36 (m, 2H), 0.90-0.94 (m, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 176.5, 173.1, 172.1, 157.0, 143.9, 143.8, 141.2, 127.4, 126.8(0), 126.7(8), 124.9, 124.8, 119.5, 66.6, 56.9, 54.2, 51.1, 47.0, 37.0, 31.1, 27.7, 24.9, 14.6, 10.4; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{33}N_3NaO_6^+$ 518.2262, found 518.2252.



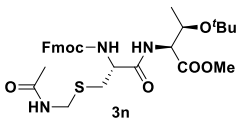
Dipeptide 3l: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (102.4 mg, 90% yield, >20:1 dr); m.p. 104-105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 6.0 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 7.5 Hz, 1H), 6.00 (d, J = 8.5 Hz, 1H), 4.57-4.62 (m, 2H), 4.40-4.46 (m, 2H), 4.24 (t, J = 7.5 Hz, 1H), 3.73 (s, 3H), 3.64 (s, 3H), 2.97 (dd, J = 17.0, 3.5 Hz, 1H), 2.60 (dd, J = 17.0, 6.0 Hz, 1H), 2.35-2.45 (m, 2H), 2.20-2.27 (m, 1H), 1.96-2.03 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 171.8, 171.4, 170.6, 156.0, 143.8, 143.7, 141.3, 127.8, 127.1, 125.1, 120.0, 82.0, 67.3, 52.6, 51.9, 51.8, 51.1, 47.1, 37.5, 29.9, 28.0, 27.2; HRMS (FTMS-

ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{36}N_2NaO_9^+$ 591.2313, found 591.2310.



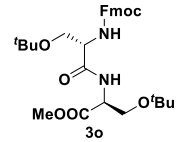
3m

Dipeptide 3m: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); Colorless oil (84.8 mg, 83% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.31 (td, J = 7.5, 1.0 Hz, 2H), 6.49 (d, J = 9.0 Hz, 1H), 5.57 (d, J = 9.0 Hz, 1H), 4.50 (dd, J = 9.0, 1.5 Hz, 1H), 4.40-4.44 (m, 1H), 4.34-4.38 (m, 1H), 4.22-4.27 (m, 2H), 4.14-4.17 (m, 1H), 3.71 (s, 3H), 2.12-2.19 (m, 1H), 1.17 (d, J = 6.0 Hz, 3H), 1.11 (s, 9H), 1.02 (dd, J = 13.0, 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 171.0, 156.3, 144.0, 143.9, 141.3, 127.7, 127.1, 125.2, 125.1, 119.9(9), 119.9(7), 74.3, 67.3, 67.1, 60.1, 57.9, 52.2, 47.2, 31.8, 28.3, 21.1, 18.9, 17.8; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{38}N_2NaO_6^+$ 533.2622, found 533.2628.



3n

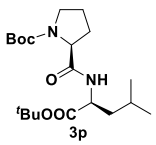
Dipeptide 3n: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); Colorless oil (98.5 mg, 84% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.61 (dd, J = 7.5, 4.0 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.35 (d, J = 9.0 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.03 (*br* s, 1H), 6.10 (d, J = 7.5 Hz, 1H), 4.61-4.64 (m, 2H), 4.47 (dd, J = 9.0, 1.5 Hz, 1H), 4.36-4.43 (m, 2H), 4.33 (dd, J = 14.0, 6.0 Hz, 1H), 4.23-4.28 (m, 2H), 3.71 (s, 3H), 3.03 (dd, J = 14.5, 6.0 Hz, 1H), 2.84 (dd, J = 14.5, 6.0 Hz, 1H), 2.02 (s, 3H), 1.20 (d, J = 6.0 Hz, 3H), 1.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1(3), 171.0(5), 170.8, 156.4, 143.8, 143.7, 141.3(1), 141.2(9), 127.8, 127.1, 125.2, 120.0, 74.3, 67.4, 67.1, 58.4, 53.8, 52.3, 47.1, 40.6, 34.1, 28.3, 23.2, 21.2; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{39}N_3NaO_7S^+$ 608.2401, found 608.2408.



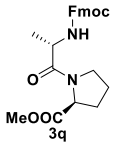
3o

Dipeptide 3o: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); Colorless oil (98.6 mg, 91% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 7.5 Hz, 1H), 7.60-7.62 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.31 (td, J = 7.5, 1.0 Hz, 2H), 5.86 (d, J = 4.5 Hz, 1H), 4.71-4.74 (m, 1H), 4.38 (d, J = 7.5 Hz, 2H), 4.30 (*br* s, 1H), 4.24 (t, J = 7.0 Hz, 1H), 3.86 (dd, J = 9.0, 3.0 Hz, 1H), 3.81 (dd, J = 8.5, 4.0 Hz, 1H), 3.74 (s, 3H), 3.56 (dd, J = 9.0, 3.0 Hz, 1H), 3.45 (t, J = 8.5 Hz, 1H), 1.26 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5(3), 170.4(5), 156.0, 144.0, 143.8, 141.3(1), 141.3(0), 127.7, 127.1, 125.2, 120.0, 74.4, 73.6, 67.1,

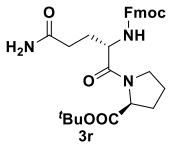
62.0, 61.8, 54.0, 53.2, 52.3, 47.2, 27.4, 27.3; HRMS (FTMS-ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{41}N_2O_7^+$ 541.2908, found 541.2900.



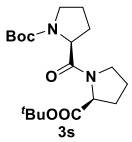
Dipeptide 3p[3]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (70.5 mg, 92% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.47-7.23 (m, 1H), 4.22-4.50 (m, 2H), 3.33-3.48 (m, 2H), 2.14-2.33 (m, 2H), 1.87 (*br* s, 2H), 1.57-1.62 (m, 2H), 1.46 (s, 19H), 0.93 (d, J = 4.0 Hz, 6H).



Dipeptide 3q[1]: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); Colorless oil (69.5 mg, 82% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.59 (dd, J = 7.5, 1.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 5.72 (d, J = 8.0 Hz, 1H), 4.51-4.57 (m, 2H), 4.34-4.35 (m, 2H), 4.21 (t, J = 7.5 Hz, 1H), 3.68-3.74 (m, 4H), 3.59-3.65 (m, 1H), 2.20-2.28 (m, 1H), 1.97-2.12 (m, 3H), 1.42 (d, J = 7.0 Hz, 3H).

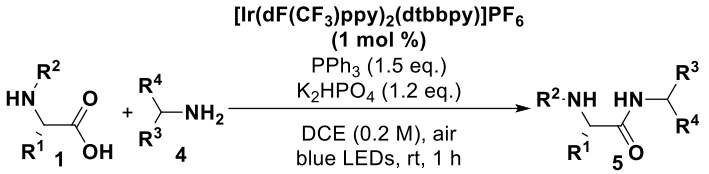


Dipeptide 3r: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); Colorless oil (80.6 mg, 77% yield, >20:1 dr); ^{1}H NMR (500 MHz, CD_3OD) δ 7.80 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.0 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.30-7.33 (m, 2H), 4.47 (dd, J = 9.0, 5.0 Hz, 1H), 4.32-4.39 (m, 3H), 4.21 (t, J = 6.5 Hz, 1H), 3.73-3.82 (m, 2H), 2.35-2.42 (m, 2H), 2.19-2.26 (m, 1H), 2.09-2.15 (m, 1H), 1.98-2.06 (m, 2H), 1.82-1.97 (m, 3H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, CD_3OD) δ 176.3, 171.5, 171.4, 157.1, 143.9, 143.8, 141.2, 127.4, 126.8, 124.9, 124.8, 119.5, 81.4, 66.6, 60.0, 52.0, 47.0, 46.9, 30.6, 28.7, 26.9, 26.8, 24.4; HRMS (FTMS-ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{36}N_3O_6^+$ 522.2599, found 522.2588.

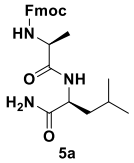


Dipeptide 3s: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); Colorless oil (59.0 mg, 80% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36-4.50 (m, 2H), 3.55-3.77 (m, 3H), 3.36-3.48 (m, 1H), 2.08-2.21 (m, 3H), 1.80-2.02 (m, 5H), 1.45 (s, 9H), 1.41 (d, J = 26.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 171.3, 170.8, 154.5, 153.8, 81.2, 81.0, 79.4, 79.4, 59.5, 57.7(4), 57.6(9), 46.8, 46.6, 46.5(1), 46.4(6), 30.0, 29.1, 28.9, 28.8, 28.5, 28.3, 28.0, 24.9, 24.8, 24.0, 23.6; HRMS (FTMS-ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{33}N_2O_5^+$ 369.2384, found 369.2392.

2.3. General procedure for the synthesis of chiral amides 5

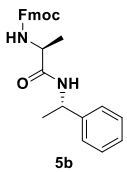


N-protected amino acids **1** (0.2 mmol, 1.0 equiv.), chiral amines **4** (0.24 mmol, 1.2 equiv.), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and K_2HPO_4 (0.24 mmol, 1.2 equiv.) were well mixed in 1,2-dichloroethane (1.0 mL). The resulting mixture was stirred at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (EtOAc/PE = 20%-40%) to yield chiral amides **5**.



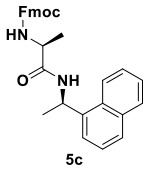
5a

Chiral amide 5a: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (71.2 mg, 84% yield, >20:1 dr); m.p. 91-92 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 7.66 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.5 Hz, 2H), 4.30 (dd, J = 8.0, 6.5 Hz, 1H), 4.24 (d, J = 7.0 Hz, 2H), 4.08 (t, J = 7.0 Hz, 1H), 4.03 (q, J = 7.0 Hz, 1H), 1.54-1.59 (m, 1H), 1.49-1.52 (m, 2H), 1.23 (d, J = 7.0 Hz, 3H), 0.81 (d, J = 6.5 Hz, 3H), 0.78 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 176.1, 174.2, 157.2, 144.0, 143.8, 141.2, 127.4, 126.8, 124.8(3), 124.8(0), 119.6, 66.6, 51.4, 50.9, 47.0, 40.5, 24.6, 22.2, 20.5, 16.6; HRMS (FTMS-ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{30}N_3O_4^+$ 424.2231, found 424.2221.

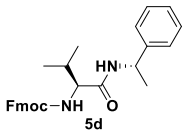


5b

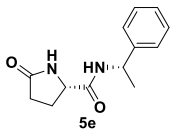
Chiral amide 5b: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (76.3 mg, 92% yield, >20:1 dr); m.p. 176-177 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.20-7.30 (m, 7H), 6.55 (d, J = 5.5 Hz, 1H), 5.56 (d, J = 6.5 Hz, 1H), 5.05-5.11 (m, 1H), 4.34 (d, J = 6.5 Hz, 2H), 4.27-4.28 (m, 1H), 4.16-4.19 (m, 1H), 1.44 (d, J = 7.0 Hz, 3H), 1.35 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 156.1, 143.7, 143.0, 141.3, 128.7, 127.8, 127.4, 127.1, 126.0, 125.0(7), 125.0(5), 120.0, 67.1, 50.5, 48.9, 47.1, 21.9, 18.9; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{26}N_2NaO_3^+$ 437.1836, found 437.1822.



Chiral amide 5c: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (87.1 mg, 94% yield, >20:1 dr); m.p. 213-214 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 7.5 Hz, 2H), 7.43 (d, J = 7.0 Hz, 2H), 7.38 (t, J = 7.5 Hz, 3H), 7.33 (t, J = 7.5 Hz, 1H), 7.26 (t, J = 7.5 Hz, 2H), 6.55 (d, J = 5.5 Hz, 1H), 5.82-5.87 (m, 1H), 5.37 (d, J = 6.0 Hz, 1H), 4.17-4.24 (m, 3H), 4.06 (t, J = 7.0 Hz, 1H), 1.62 (d, J = 7.0 Hz, 3H), 1.38 (d, J = 5.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 156.0, 143.8, 143.7, 141.3(0), 141.2(8), 138.0, 133.9, 131.0, 128.8, 128.4, 127.8, 127.1, 126.5, 125.8, 125.2, 125.0, 123.2, 122.5, 120.0, 67.1, 50.5, 47.1, 44.9, 20.8, 18.5; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{28}N_2NaO_3^+$ 487.1992, found 487.1973.

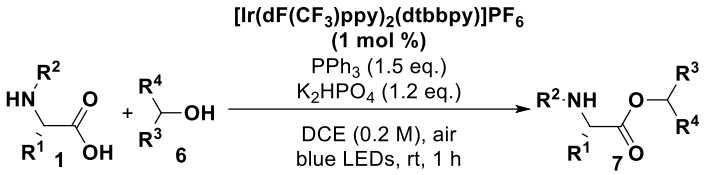


Chiral amide 5d: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); White solid (75.1 mg, 85% yield, >20:1 dr); m.p. 180-181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.55-7.58 (m, 2H), 7.39 (t, J = 7.0 Hz, 2H), 7.30-7.31 (m, 6H), 7.22-7.26 (m, 1H), 6.19 (d, J = 6.5 Hz, 1H), 5.46 (d, J = 8.5 Hz, 1H), 5.08-5.14 (m, 1H), 4.39-4.43 (m, 1H), 4.33-4.36 (m, 1H), 4.17-4.22 (m, 1H), 3.94 (t, J = 7.0 Hz, 1H), 2.03-2.09 (m, 1H), 1.47 (d, J = 7.0 Hz, 3H), 0.89 (d, J = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 156.5, 143.8(3), 143.7(8), 142.9, 141.3, 128.7(3), 128.6(8), 127.8, 127.5, 127.1, 126.1, 125.1(1), 125.0(5), 120.0, 67.1, 60.6, 49.0, 47.2, 31.3, 21.7, 19.2, 18.0; HRMS (FTMS-ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{31}N_2O_3^+$ 443.2329, found 443.2352.

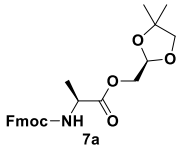


Chiral amide 5e: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-40% (v/v); Colorless oil (37.6 mg, 81% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.34 (m, 4H), 7.24-7.27 (m, 1H), 6.85 (s, 1H), 6.77 (d, J = 7.5 Hz, 1H), 5.07-5.13 (m, 1H), 4.08 (dd, J = 9.0, 5.0 Hz, 1H), 2.44-2.51 (m, 1H), 2.24-2.33 (m, 2H), 2.11-2.18 (m, 1H), 1.48 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 171.1, 142.8, 128.7, 127.5, 126.3, 57.1, 49.0, 29.3, 25.8, 21.6; HRMS (FTMS-ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}N_2O_2^+$ 233.1285, found 233.1284.

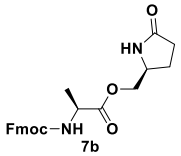
2.4. General procedure for the synthesis of chiral esters 7



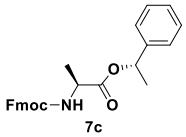
N-protected amino acids **1** (0.2 mmol, 1.0 equiv.), chiral alcohols **6** (0.24 mmol, 1.2 equiv.), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and K_2HPO_4 (0.24 mmol, 1.2 equiv.) were well mixed in 1,2-dichloroethane (1.0 mL). The resulting mixture was stirred at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (EtOAc/PE = 20%-30%) to yield chiral esters **7**.



Chiral ester 7a: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-30% (v/v); Colorless oil (76.5 mg, 90% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 6.5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 5.43 (d, J = 7.5 Hz, 1H), 4.35-4.45 (m, 3H), 4.28-4.32 (m, 1H), 4.17-4.22 (m, 3H), 4.03-4.06 (m, 1H), 3.71-3.74 (m, 1H), 1.44 (d, J = 7.0 Hz, 3H), 1.42 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 155.7, 143.9, 143.8, 141.3, 127.8, 127.1, 125.1, 120.0, 109.9, 73.4, 67.0, 66.2, 65.5, 49.7, 47.2, 26.7, 25.3, 18.6; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{27}NNaO_6^+$ 448.1731, found 448.1721.

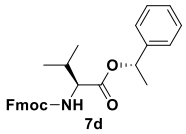


Chiral ester 7b: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-30% (v/v); Colorless oil (76.1 mg, 93% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (*br* s, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.58-7.60 (m, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 6.21 (d, J = 8.0 Hz, 1H), 4.39-4.48 (m, 2H), 4.32-4.36 (m, 2H), 4.22 (t, J = 7.0 Hz, 1H), 3.92-3.94 (m, 1H), 3.80 (t, J = 9.8 Hz, 1H), 2.28-2.40 (m, 2H), 2.14-2.22 (m, 1H), 1.62-1.69 (m, 1H), 1.44 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.0, 172.6, 156.1, 143.9, 143.8, 141.3, 127.7, 127.0(9), 127.0(8), 125.2, 125.1, 120.0(3), 120.0(2), 68.0, 66.9, 52.9, 50.0, 47.2, 29.8, 22.8, 18.5; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{24}N_2NaO_5^+$ 431.1577, found 431.1575.

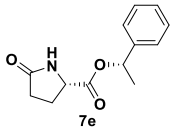


Chiral ester 7c: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-30% (v/v); Colorless oil (73.1 mg, 88% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J =

7.5 Hz, 2H), 7.58-7.60 (m, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.27-7.36 (m, 7H), 5.91 (q, J = 6.5 Hz, 1H), 5.35 (d, J = 7.5 Hz, 1H), 4.34-4.46 (m, 3H), 4.21 (t, J = 7.0 Hz, 1H), 1.57 (d, J = 6.5 Hz, 3H), 1.39 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 155.7, 144.0, 143.8, 141.3, 141.2, 128.6, 128.1, 127.8, 127.1, 126.0, 125.2, 125.1, 120.0, 73.8, 67.1, 49.7, 47.2, 22.3, 18.6; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{25}NNaO_4^+$ 438.1676, found 438.1674.

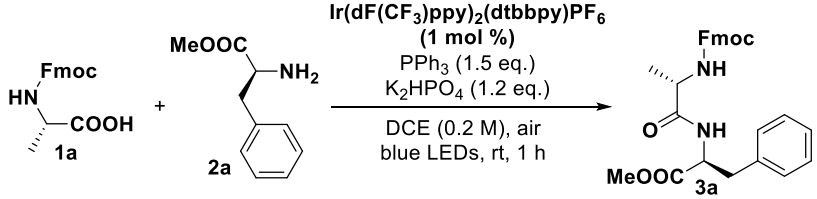


Chiral ester 7d: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-30% (v/v); Colorless oil (80.1 mg, 90% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.26-7.39 (m, 9H), 5.93 (q, J = 6.5 Hz, 1H), 5.35 (d, J = 9.0 Hz, 1H), 4.35-4.39 (m, 3H), 4.21 (t, J = 7.0 Hz, 1H), 2.14-2.20 (m, 1H), 1.56 (d, J = 6.5 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H), 0.73 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 156.4, 144.0, 143.9, 141.4, 141.0, 128.6, 128.2, 127.8, 127.1, 126.3, 125.2, 120.0(4), 120.0(3), 73.7, 67.1, 59.0, 47.3, 31.3, 22.1, 19.1, 17.2; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{29}NNaO_4^+$ 466.1989, found 466.1967.



Chiral ester 7e: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-30% (v/v); Colorless oil (38.6 mg, 83% yield, >20:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.37 (m, 4H), 7.28-7.32 (m, 1H), 6.71 (s, 1H), 5.93 (q, J = 6.5 Hz, 1H), 4.24-4.26 (m, 1H), 2.41-2.48 (m, 1H), 2.27-2.38 (m, 2H), 2.10-2.17 (m, 1H), 1.56 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 171.3, 140.9, 128.7, 128.2, 126.1, 73.8, 55.6, 29.2, 24.7, 22.1; HRMS (FTMS-ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}NO_3^+$ 234.1125, found 234.1122.

2.5. Synthetic procedure of 5 mmol scale model reaction



N-protected amino acid **1a** (1.56 g, 5.0 mmol, 1.0 equiv.), amino acid ester **2a** (1.08 g, 6.0 mmol, 1.2 equiv.), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (56.1 mg, 0.05 mmol, 1 mol %), PPh_3 (1.97 g, 7.5 mmol, 1.5 equiv.) and K_2HPO_4 (1.05 g, 6.0 mmol, 1.2 equiv.) were well mixed in 1,2-dichloroethane (25.0 mL). The resulting mixture was stirred at room

temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (EtOAc/PE = 20%-40%) to yield dipeptide **3a** in 84% yield (1.98 g, white solid) with >20:1 dr.

2.6. Experimental set-up (Figure S1)

Photochemical reactions were performed with a LED flow reactor WP-TEC-1020HSL (WATTCAS, China). Light flux: Φ (1 m) = 134.53 lm.

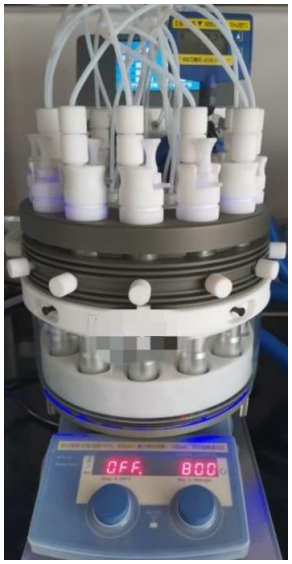


Figure S1. The set-up for the reaction

2.7. UV/Vis Absorption Experiments (Figure S2)

UV/Vis absorption spectra of reaction mixtures before, during and after reaction were recorded in 1 cm path quartz cuvettes using a Shimadzu UV-2600 (Figure S2).

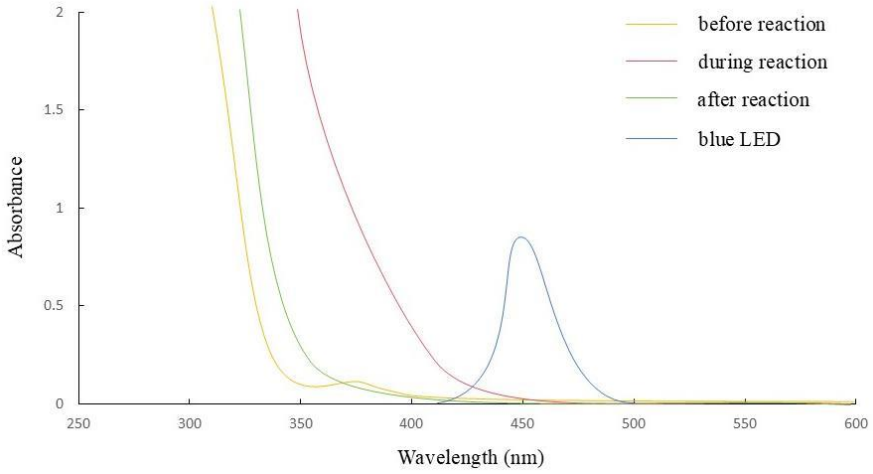
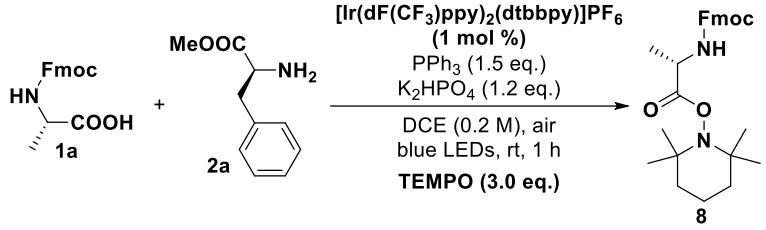
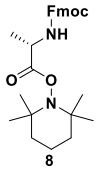


Figure S2. UV/Vis absorption spectrometry of the mixtures

2.8. Mechanistic experiments

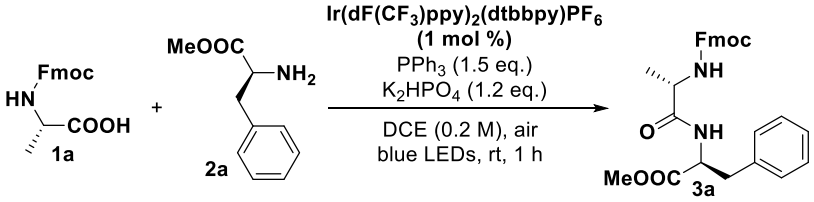


N-protected amino acid **1a** (0.2 mmol, 1.0 equiv.), amino acid ester **2a** (0.24 mmol, 1.2 equiv.), Ir(dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.), K_2HPO_4 (0.24 mmol, 1.2 equiv.) and TEMPO (0.6 mmol, 3.0 equiv.) were well mixed in 1,2-dichloroethane (1.0 mL). The resulting mixture was stirred at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (EtOAc/PE = 20%-30%) to yield radical-trapping product **8**.



Radical-trapping product 8: Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 20%-30% (v/v); Colorless oil (73.7 mg, 82% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.59-7.61 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 5.56 (d, J = 6.5 Hz, 1H), 5.52 (d, J = 6.5 Hz, 1H), 5.40 (d, J = 7.5 Hz, 1H), 4.35-4.45 (m, 3H), 4.22 (t, J = 7.0 Hz, 1H), 1.43-1.50 (m, 7H), 1.16 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 155.6, 143.9, 143.8, 141.3, 127.7, 127.1, 125.1, 120.0, 95.1, 67.0, 59.9, 59.8, 49.8, 47.2, 39.7, 33.3(0), 33.2(5), 20.2, 18.7, 17.1; HRMS (FTMS-ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{34}N_2NaO_4^+$ 473.2411, found 473.2436.

2.9. Experiment supporting catalyst regeneration mechanism



N-protected amino acid **1a** (0.2 mmol, 1.0 equiv.), amino acid ester **2a** (0.24 mmol, 1.2 equiv.), Ir(dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (1 mol %), PPh_3 (0.3 mmol, 1.5 equiv.) and K_2HPO_4 (0.24 mmol, 1.2 equiv.) were well mixed in 1,2-dichloroethane (1.0 mL). The resulting mixture was stirred at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). Then, N-protected amino acid **1a** (0.2 mmol, 1.0 equiv.), amino acid ester **2a** (0.24 mmol, 1.2 equiv.), PPh_3 (0.3 mmol, 1.5 equiv.), K_2HPO_4 (0.24 mmol,

1.2 equiv.) and 1,2-dichloroethane (1.0 mL) were added. The resulting mixture was stirred at room temperature for 1 h under the irradiation of 440 nm blue LEDs (10 W). The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (EtOAc/PE = 20%-30%) to yield dipeptide **3a** in 88% yield (166.7 mg, white solid) with >20:1 dr.

References

(1) S. Sharma, N. W. Buchbinder, W. M. Braje, S. Handa, Fast Amide Couplings in Water: Extraction, Column Chromatography, and Crystallization not Required. *Org. Lett.*, 2020, **22**, 5737-5740.

(2) H. Li, X. Jiang, Y. Ye, C. Fan, T. Romoff, M. Goodman, 3-(Diethoxyphosphoryloxy)-1,2,3-Benzotriazin-4(3H)-One (DEPBT): A New Coupling Reagent with Remarkable Resistance to Racemization. *Org. Lett.*, 1999, **1**, 91-93.

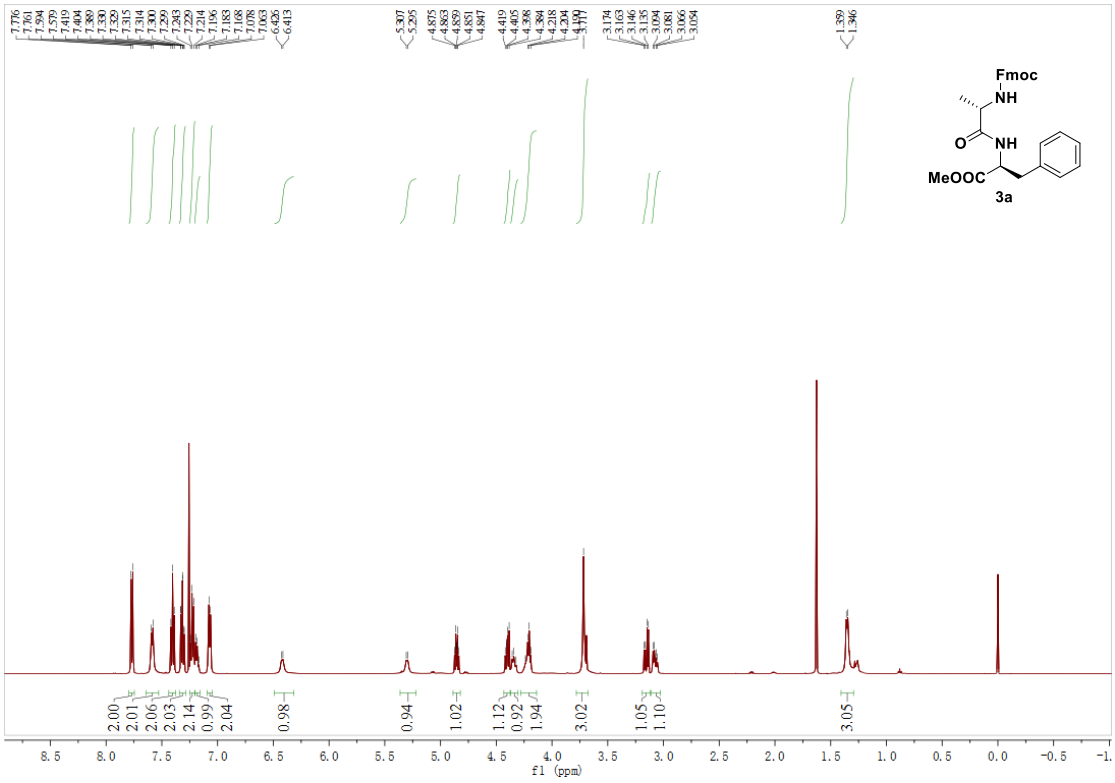
(3) E. Suárez-Picado, E. Quiñoá, R. Riguera, F. Freire, Chiral Overpass Induction in Dynamic Helical Polymers Bearing Pendant Groups with Two Chiral Centers. *Angew. Chem., Int. Ed.*, 2020, **59**, 4537-4543.

(4) L. Hu, S. Xu, Z. Zhao, Y. Yang, Z. Peng, M. Yang, C. Wang, J. Zhao, Ynamides as Racemization-Free Coupling Reagents for Amide and Peptide Synthesis. *J. Am. Chem. Soc.*, 2016, **138**, 13135-13138.

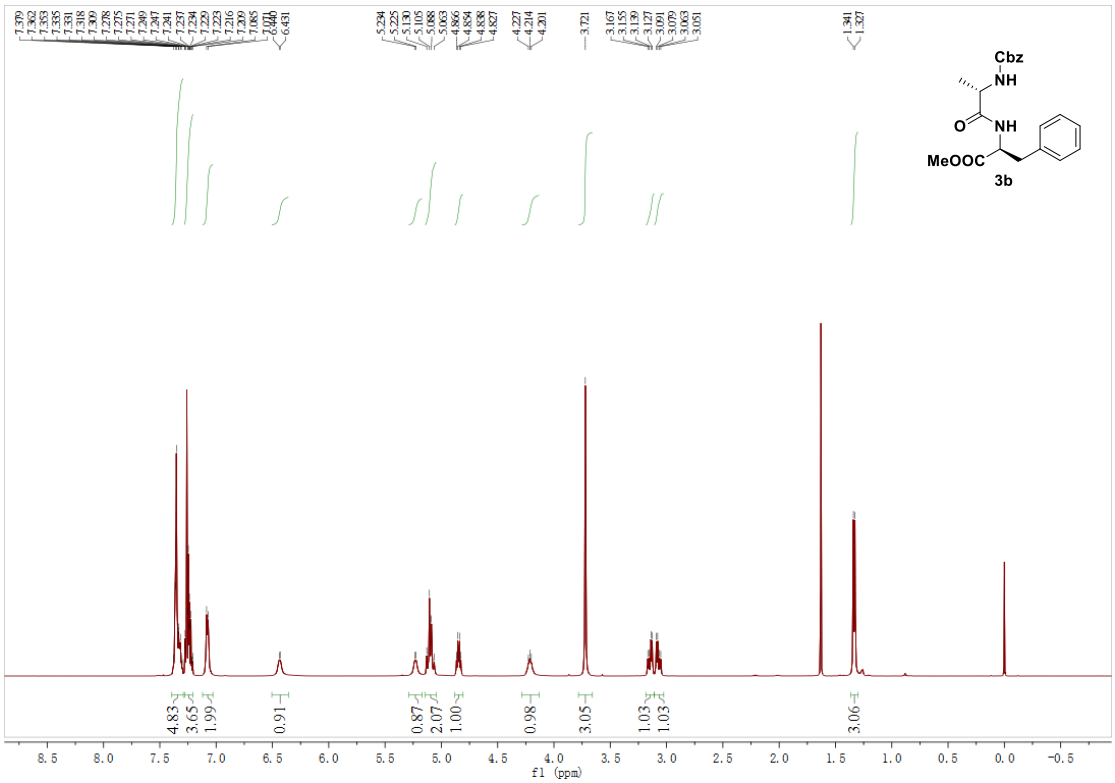
(5) J.-W. Ren, M.-N. Tong, Y.-F. Zhao, F. Ni, Synthesis of Dipeptide, Amide, and Ester without Racemization by Oxalyl Chloride and Catalytic Triphenylphosphine Oxide. *Org. Lett.*, 2021, **23**, 7497-7502.

3. NMR Spectra

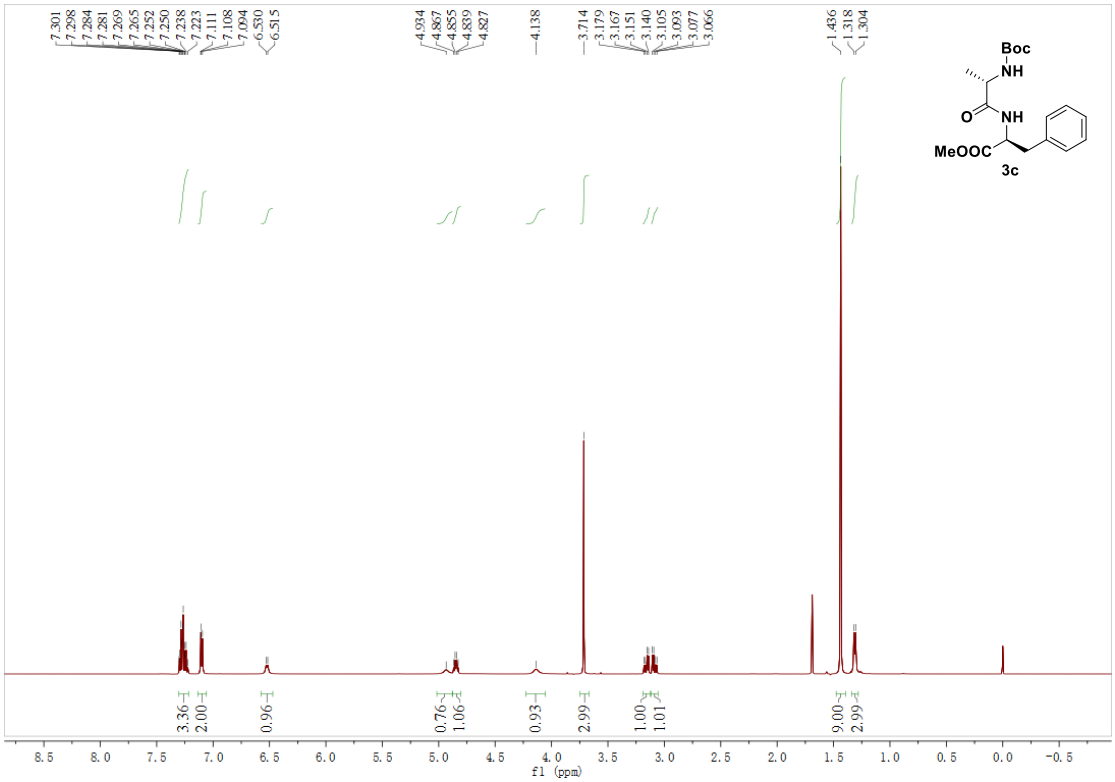
500 MHz, $CDCl_3$, ^1H NMR



500 MHz, $CDCl_3$, ^1H NMR



500 MHz, $CDCl_3$, ^1H NMR



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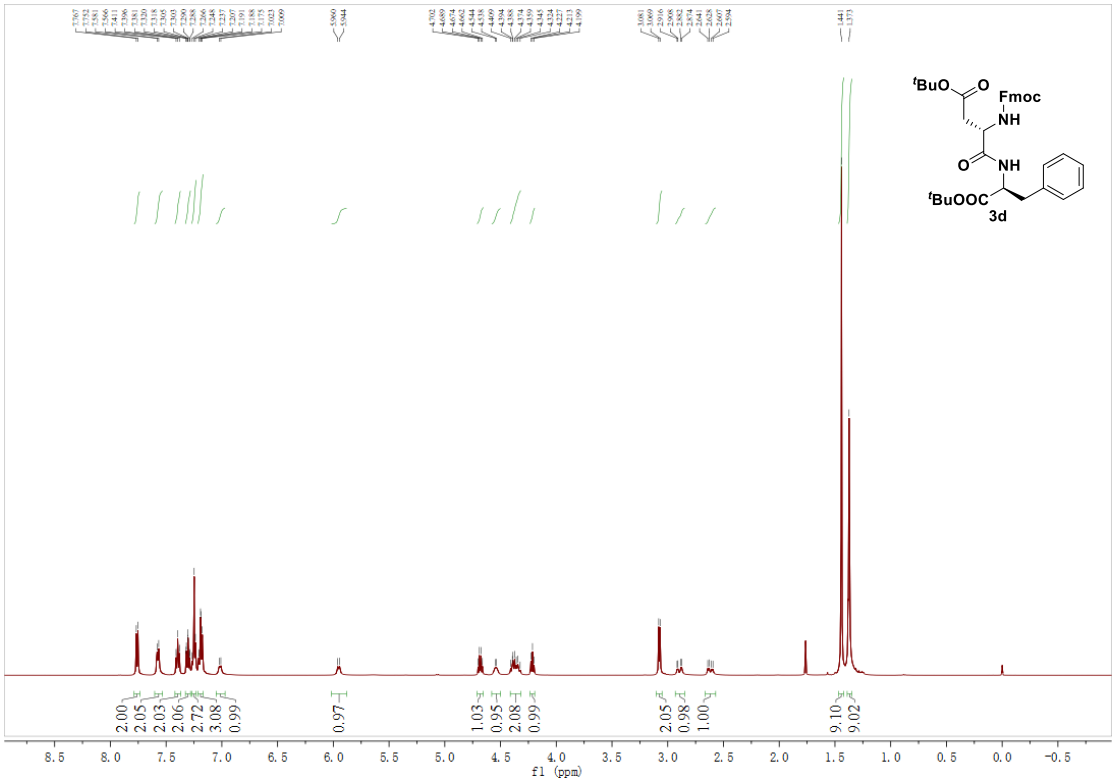
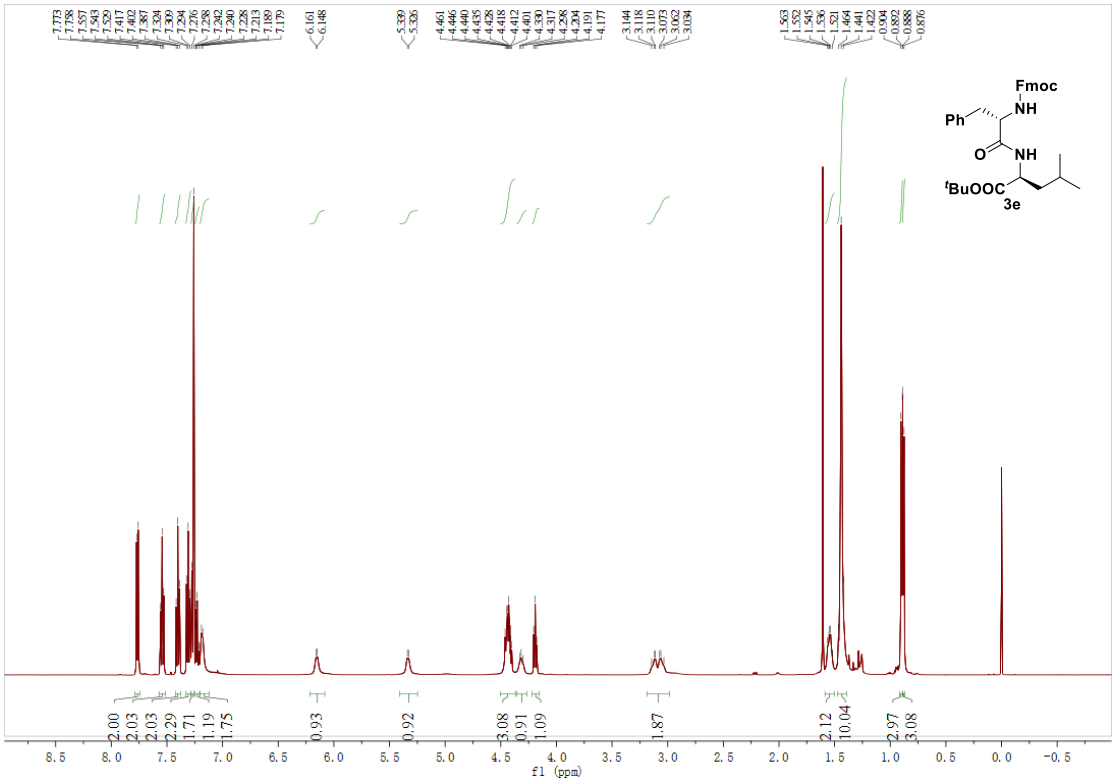


500 MHz, $CDCl_3$, ^1H NMR



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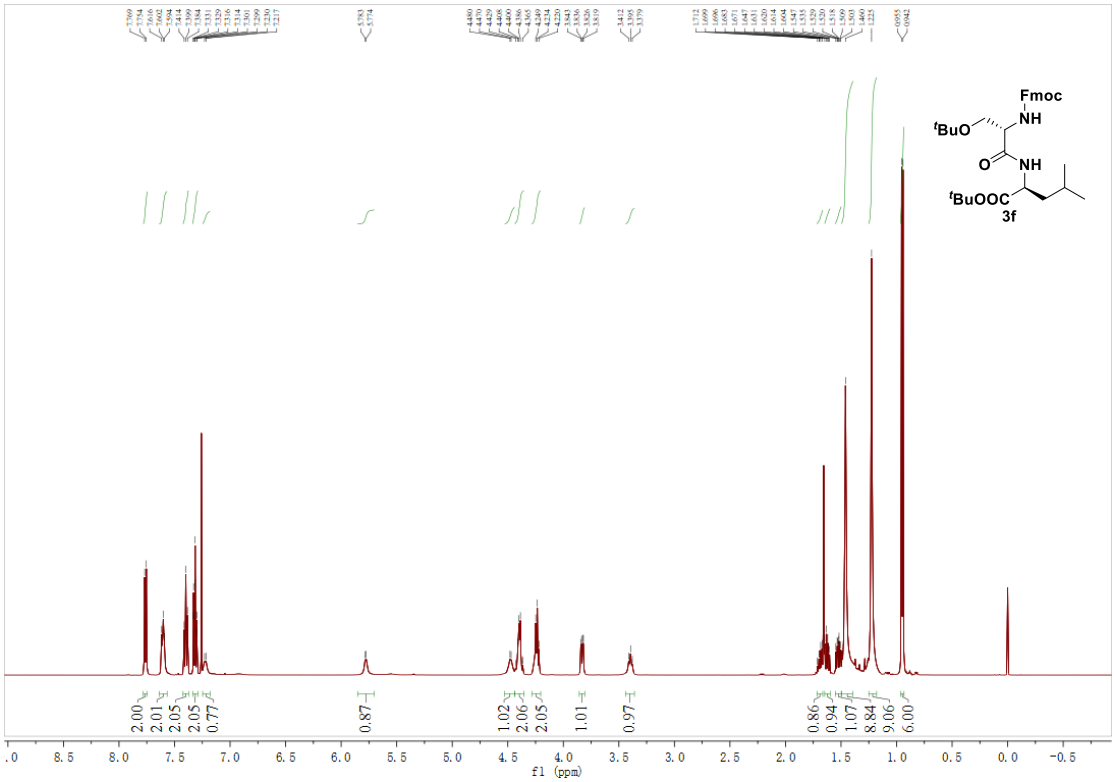

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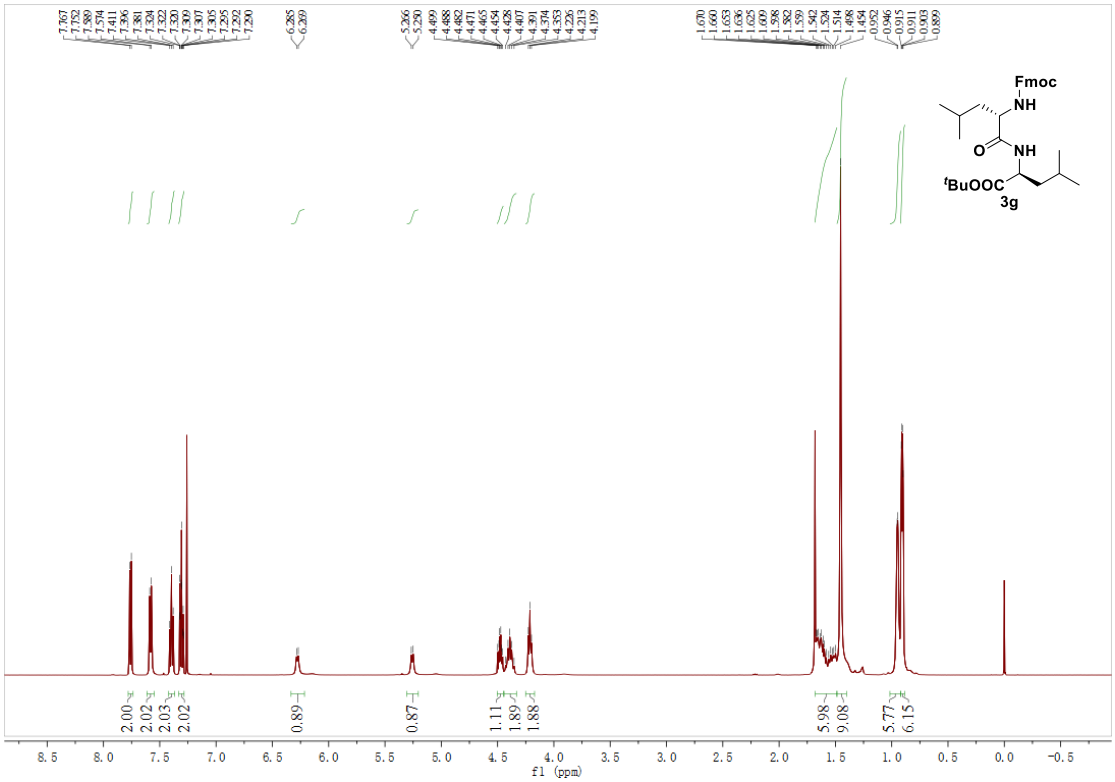

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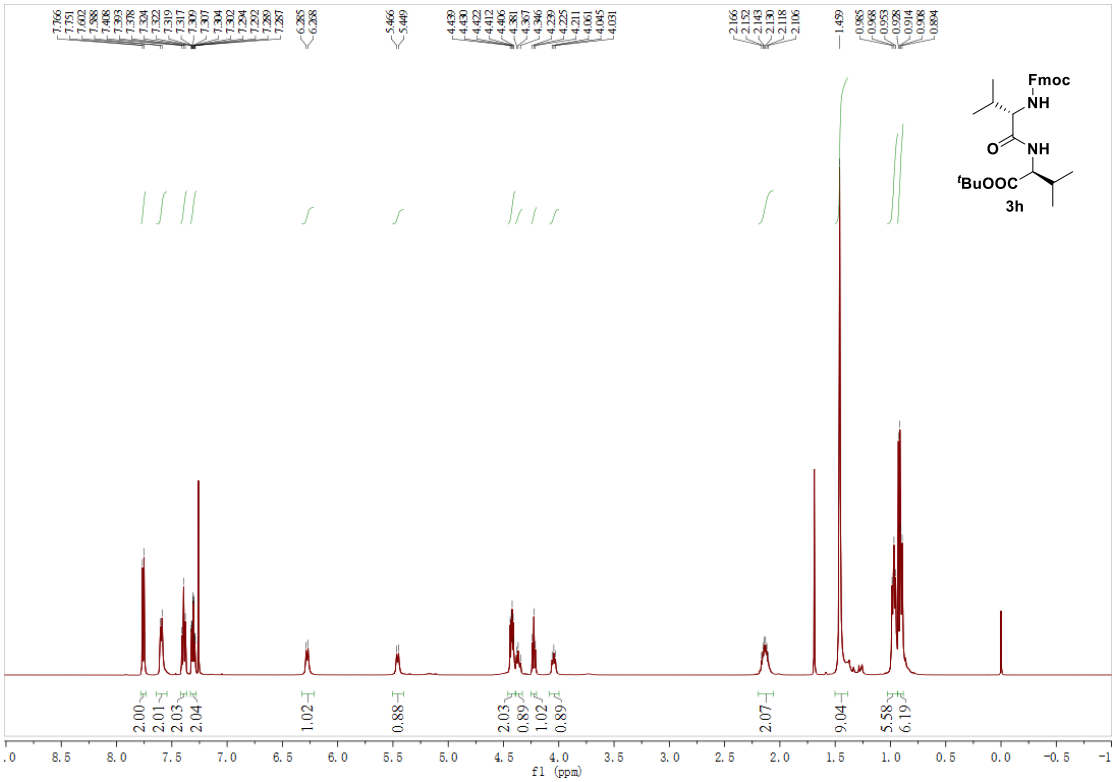

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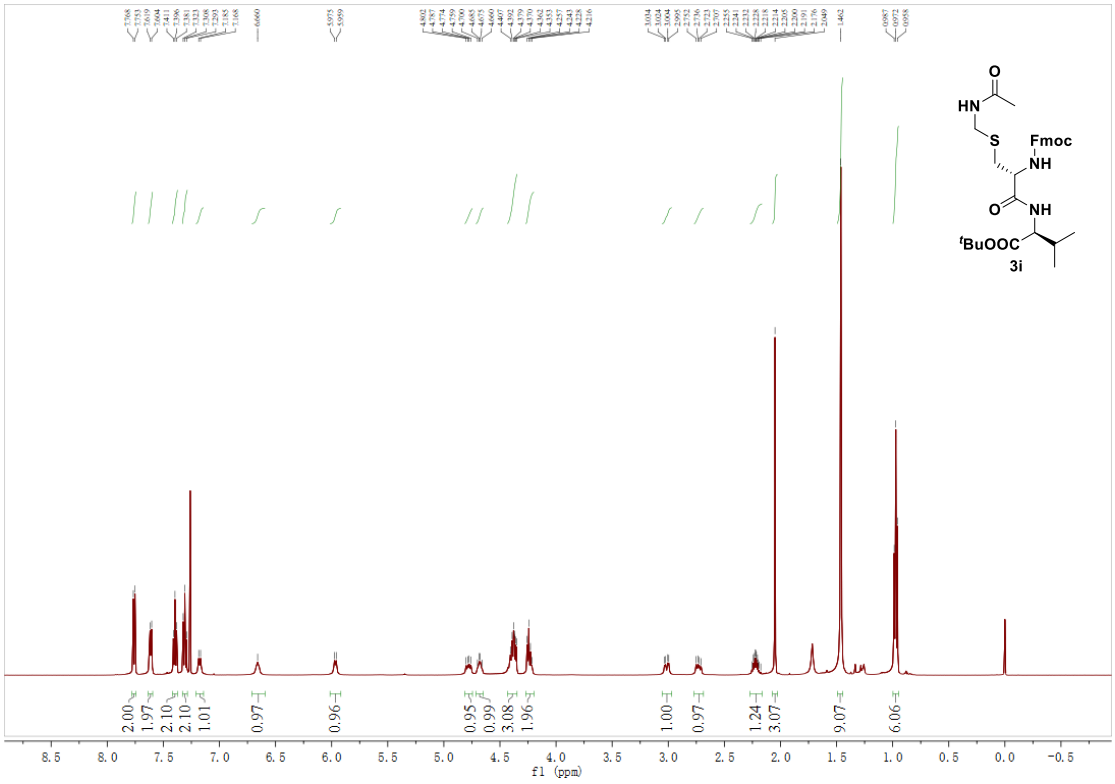
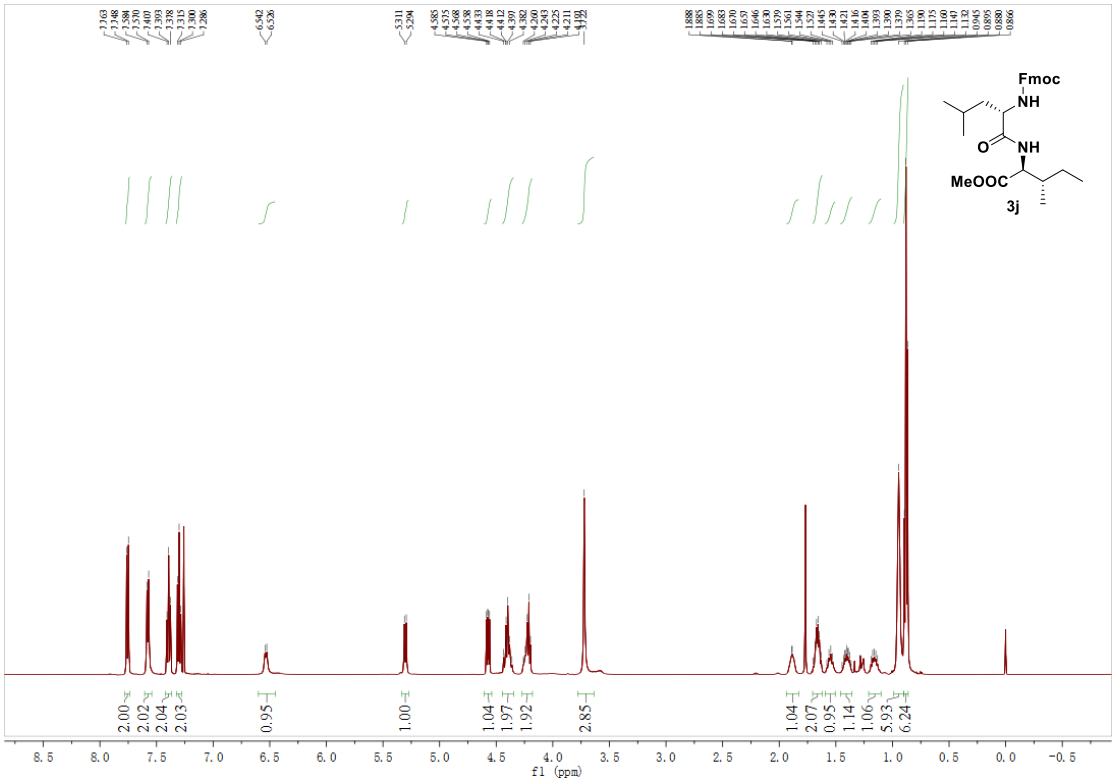


500 MHz, $CDCl_3$, ^1H NMR



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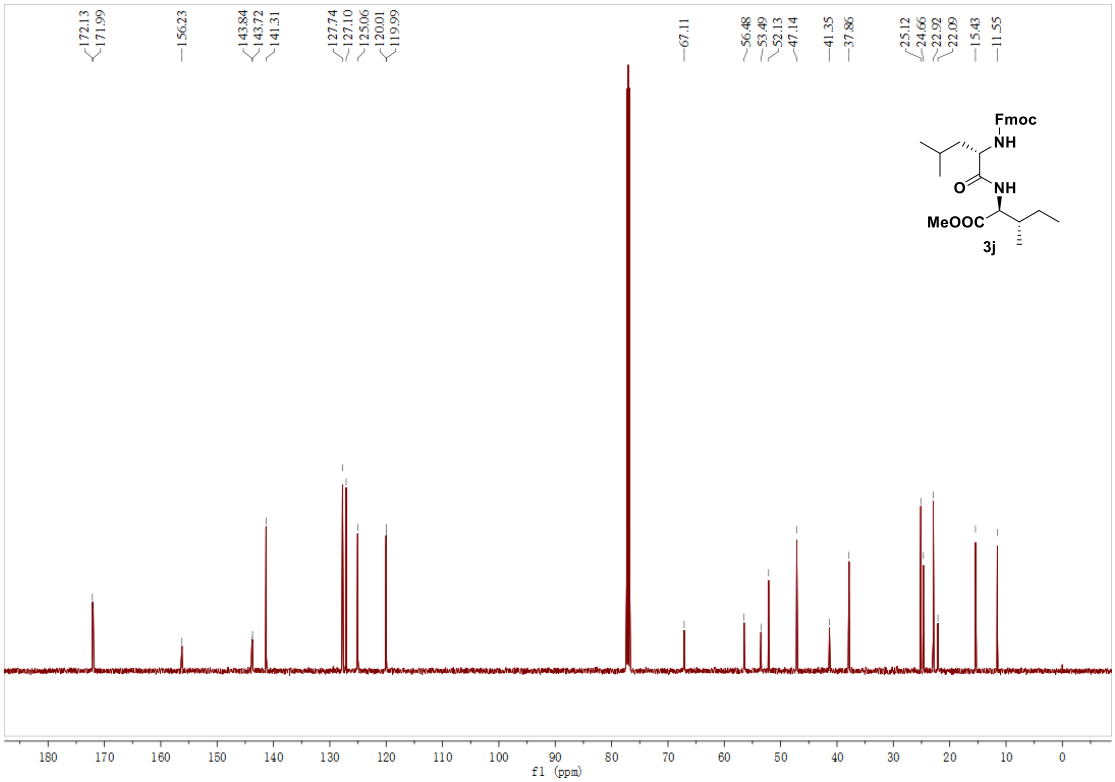
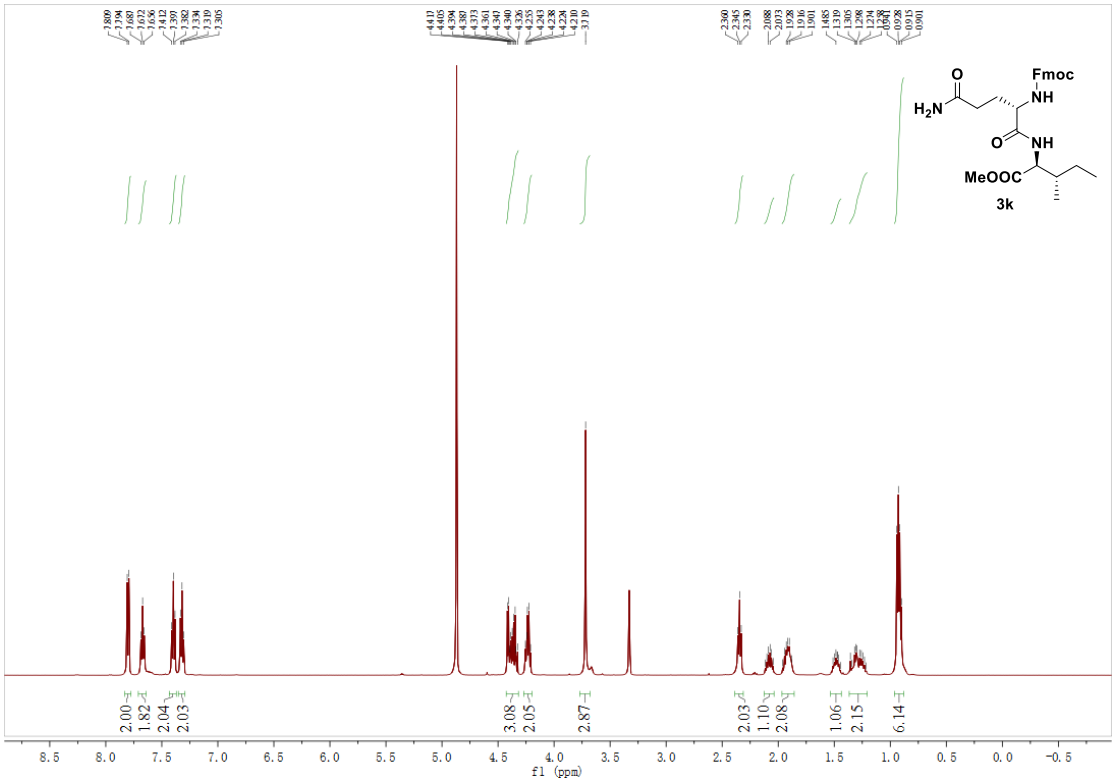
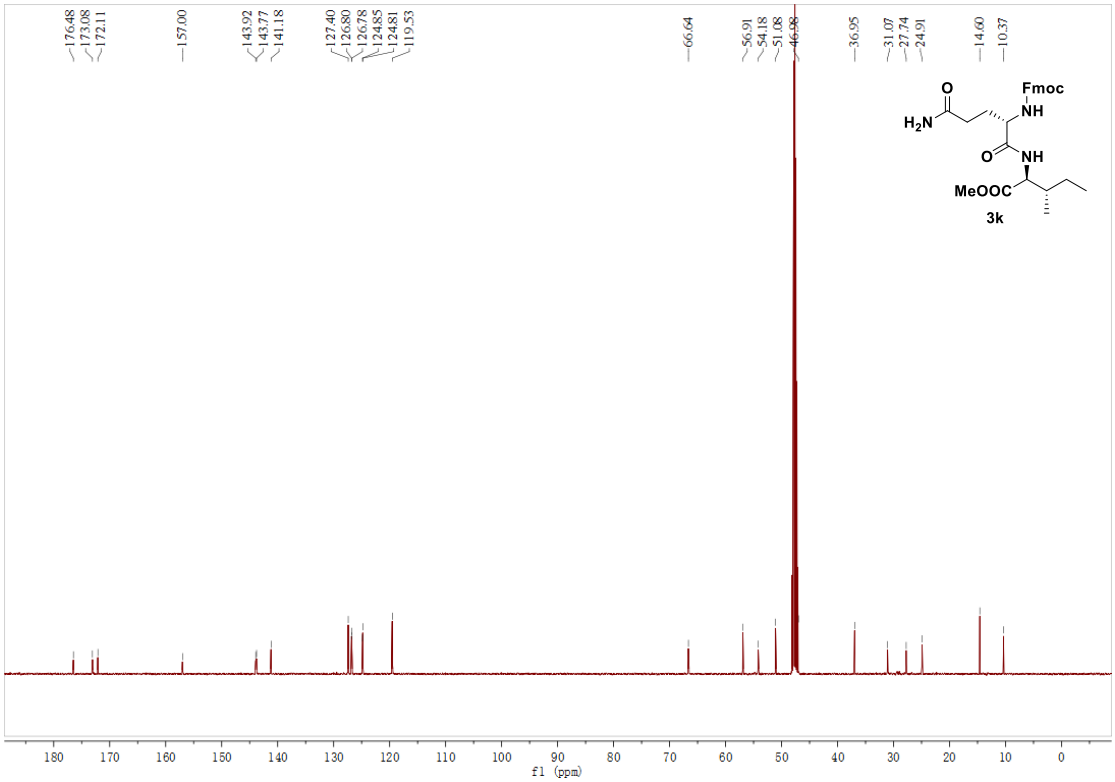


500 MHz, CD_3OD, ^1H NMR



125 MHz, CD_3OD, ^{13}C NMR



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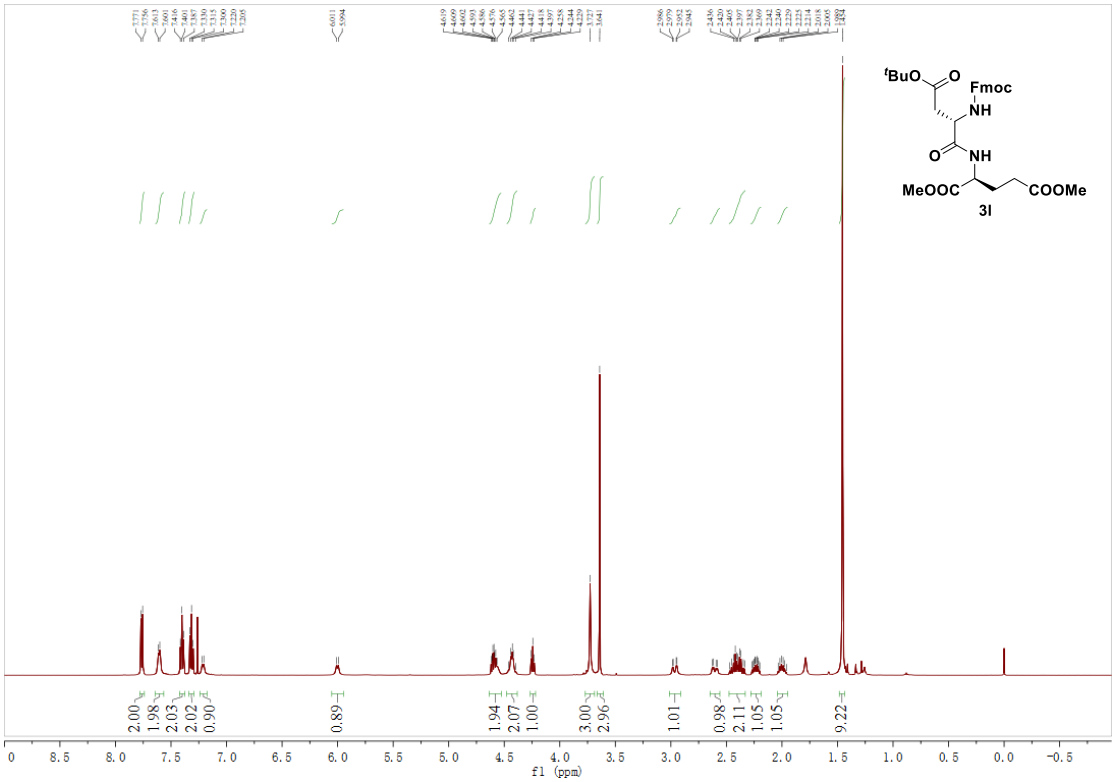
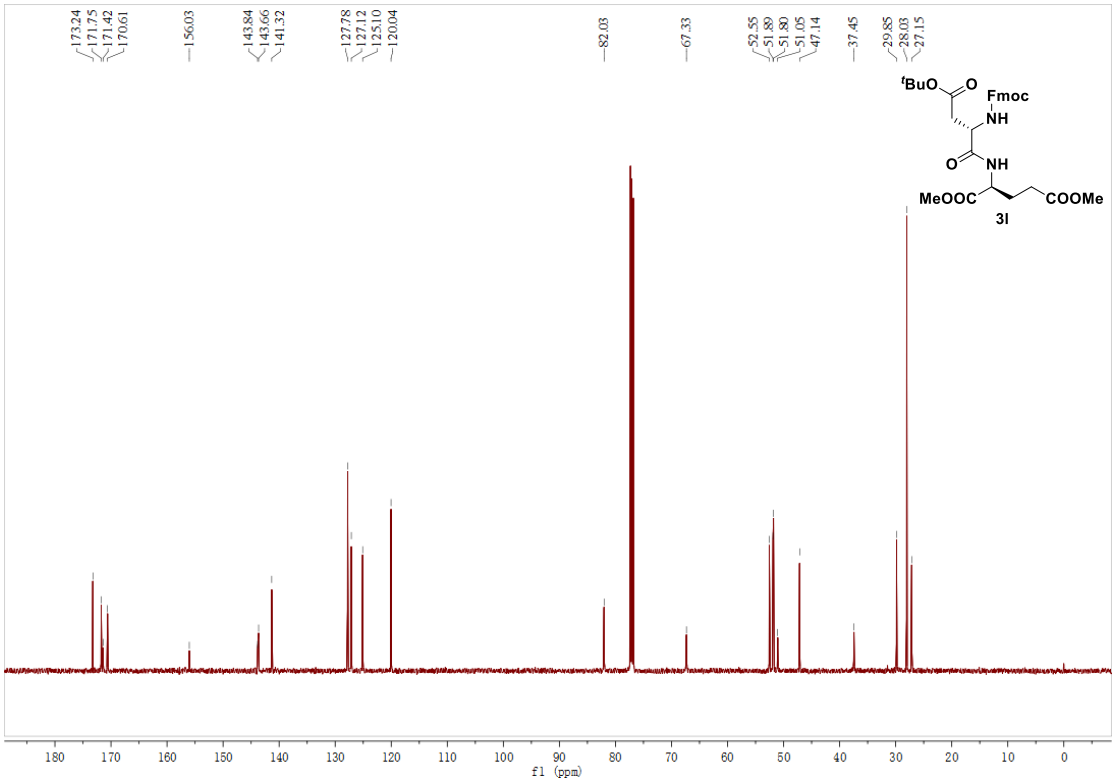


125 MHz, $CDCl_3$, ^{13}C NMR



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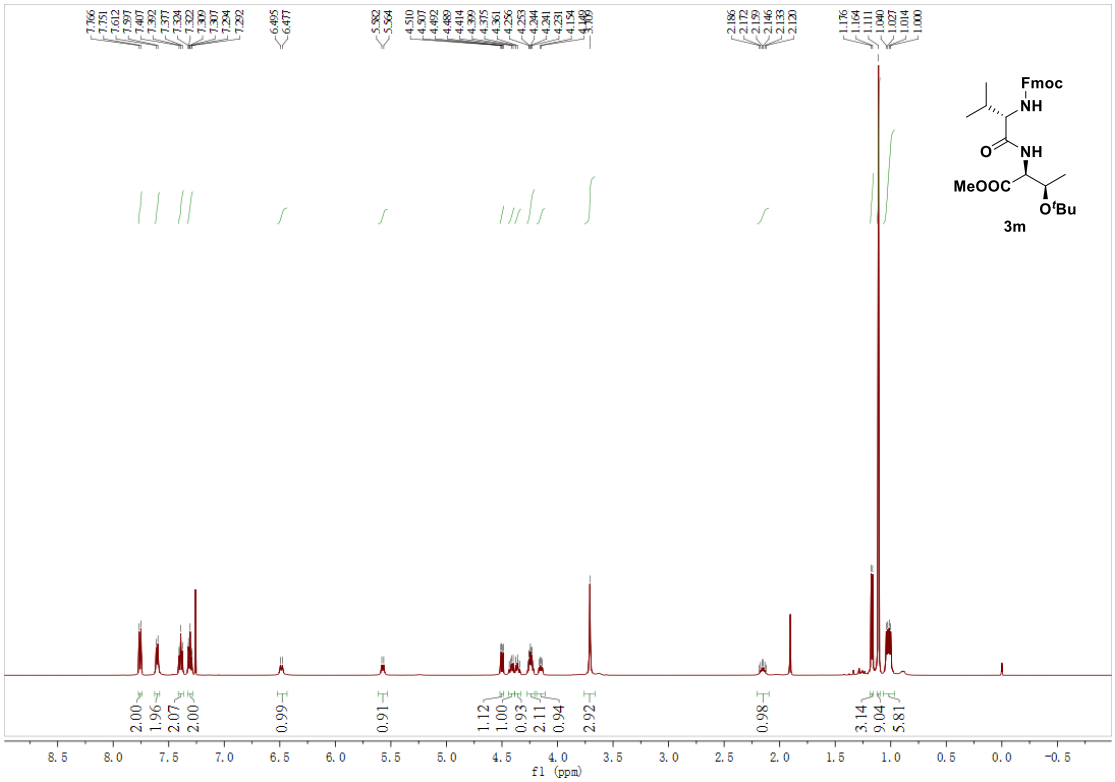
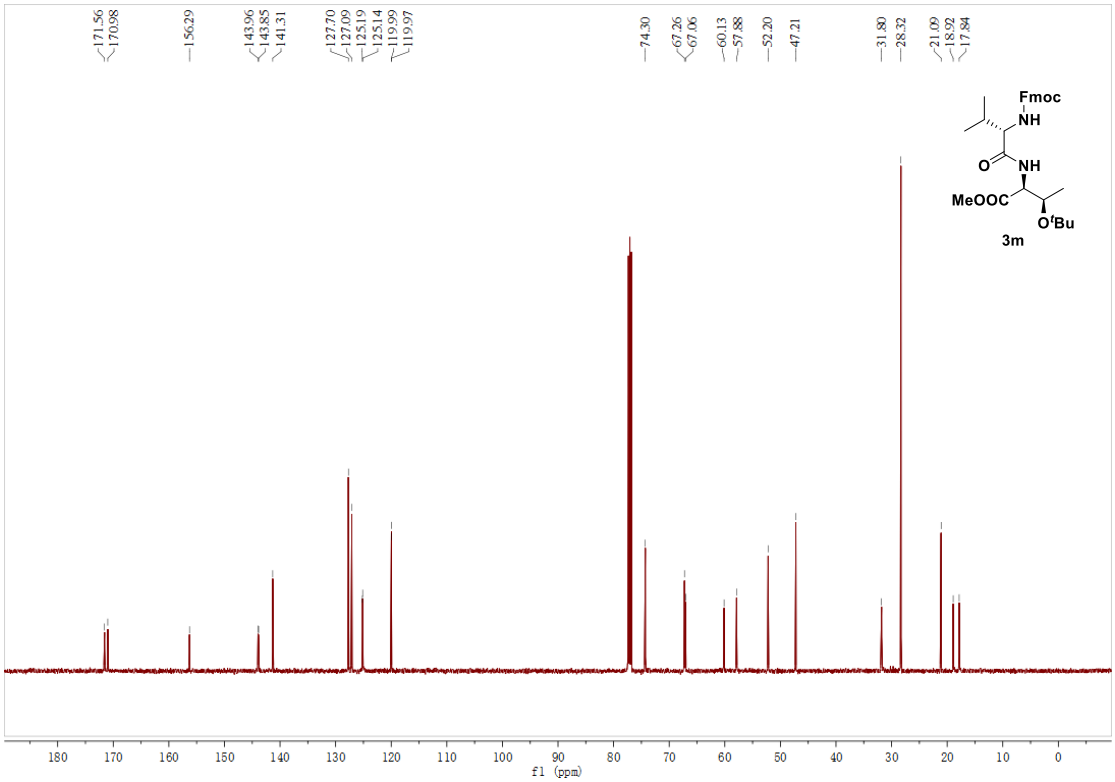
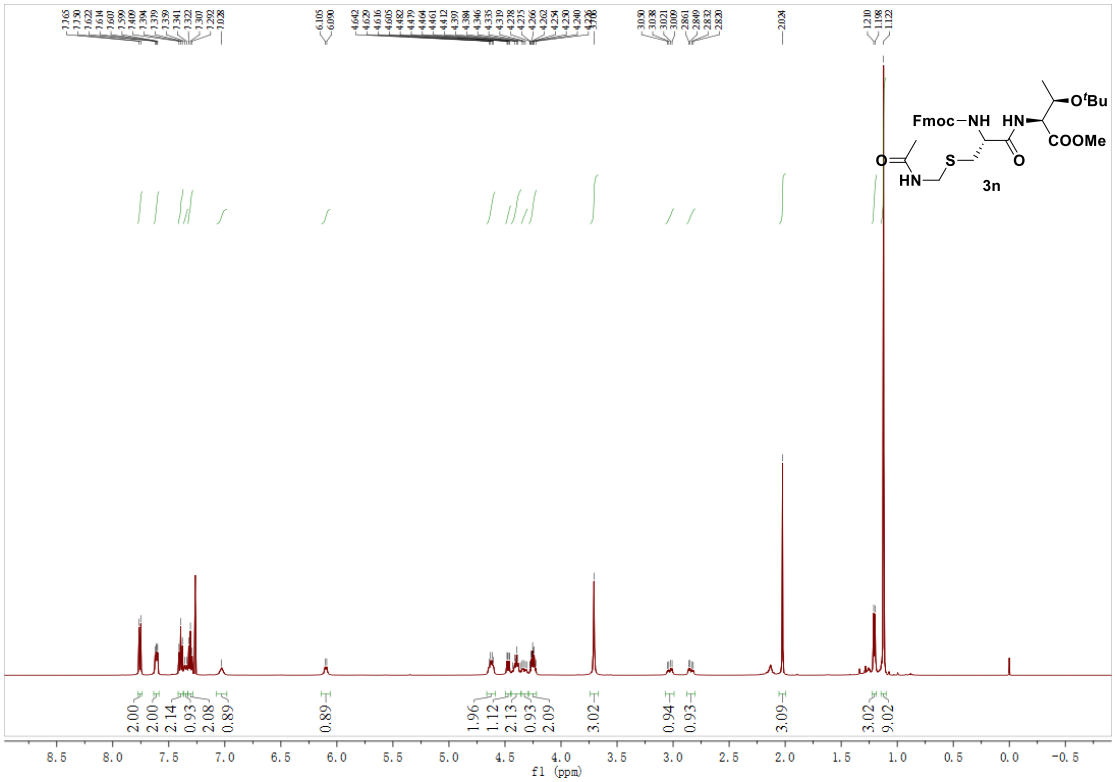


125 MHz, $CDCl_3$, ^{13}C NMR



500 MHz, $CDCl_3$, ^1H NMR



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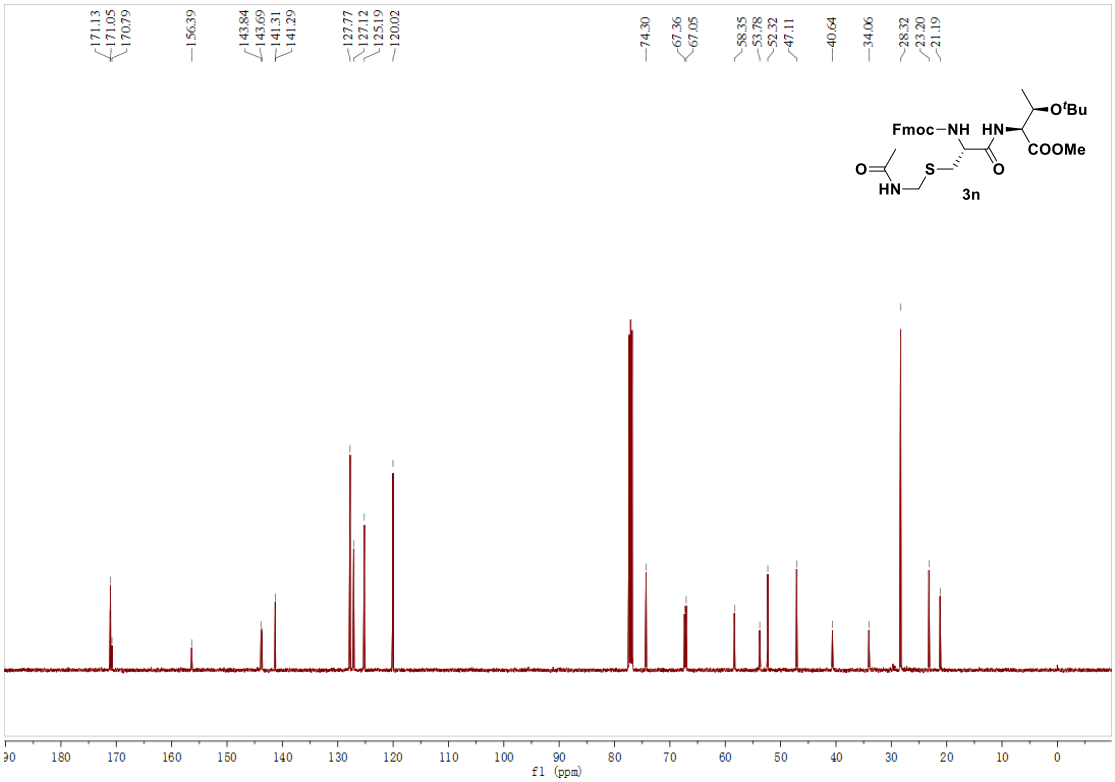
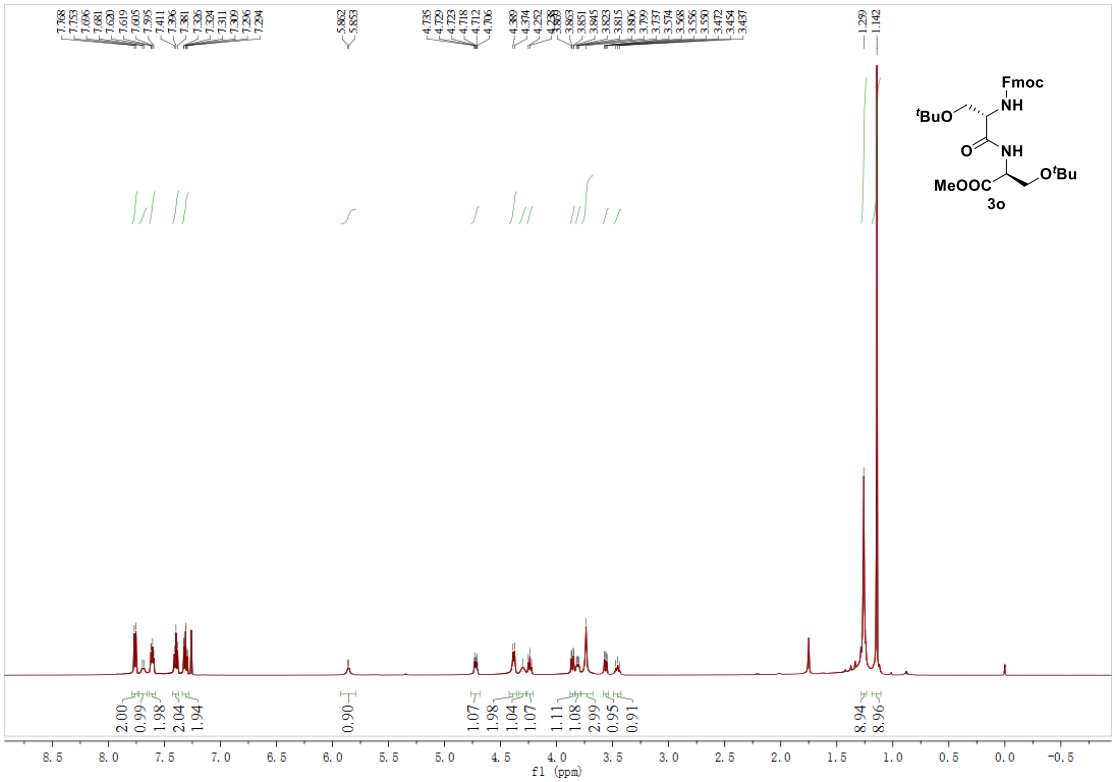
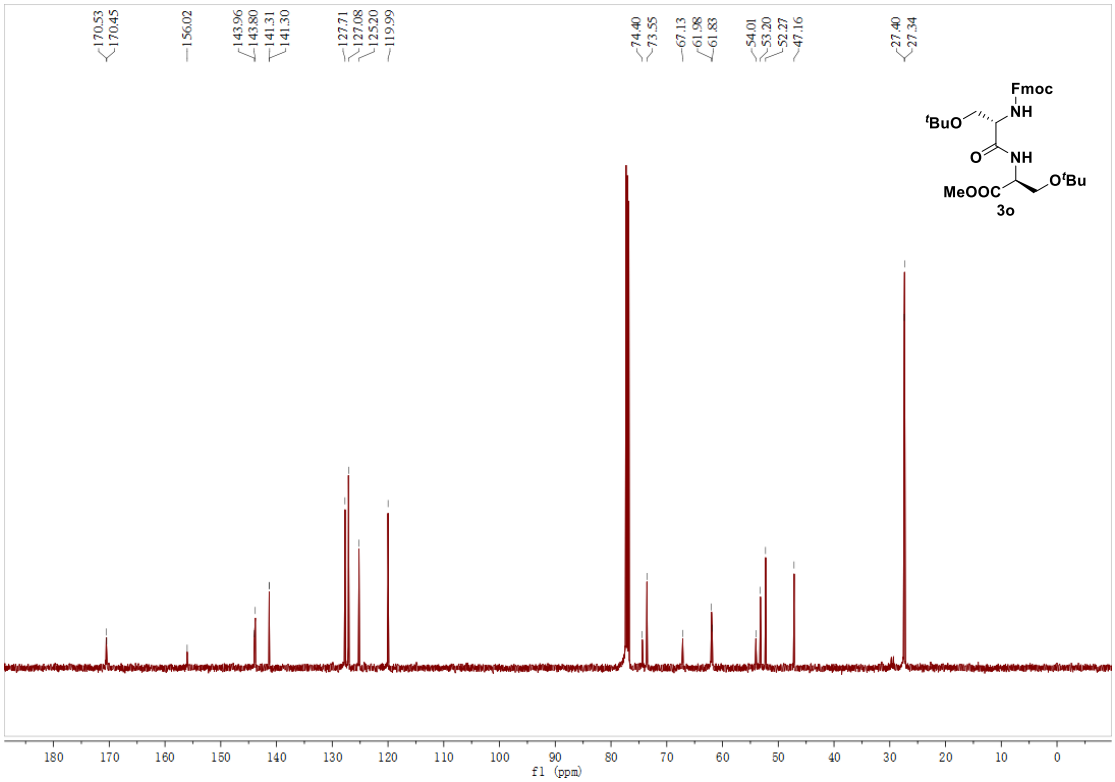


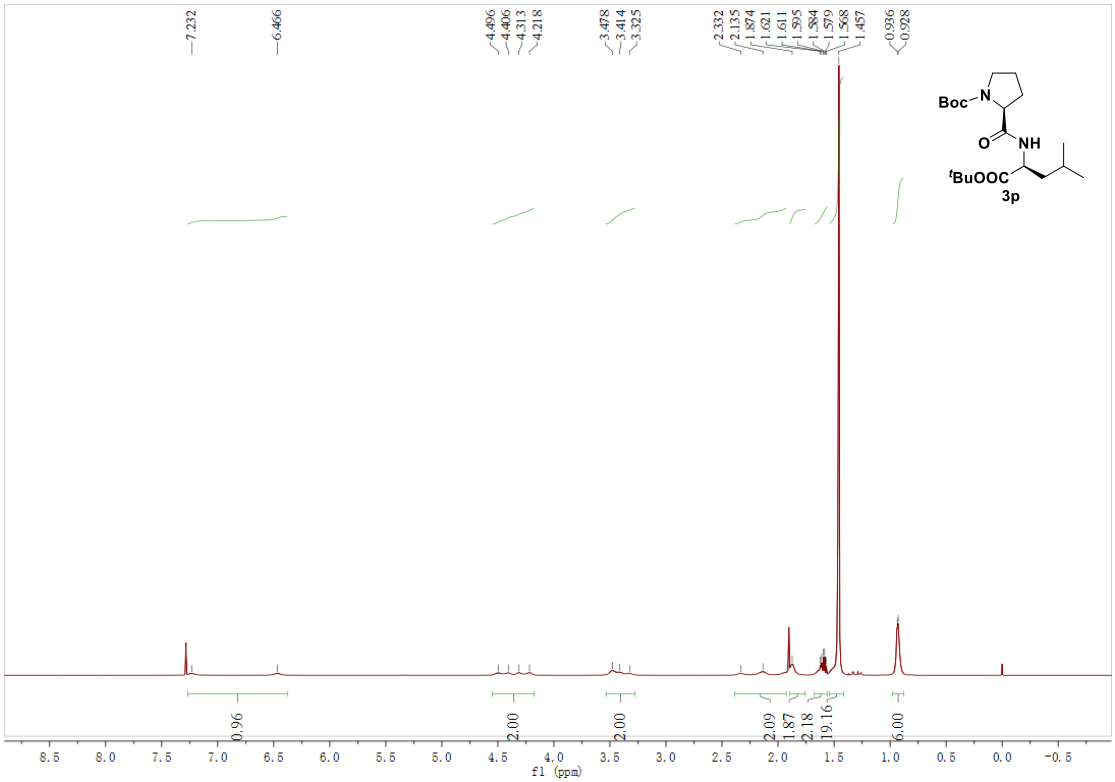
500 MHz, $CDCl_3$, ^1H NMR



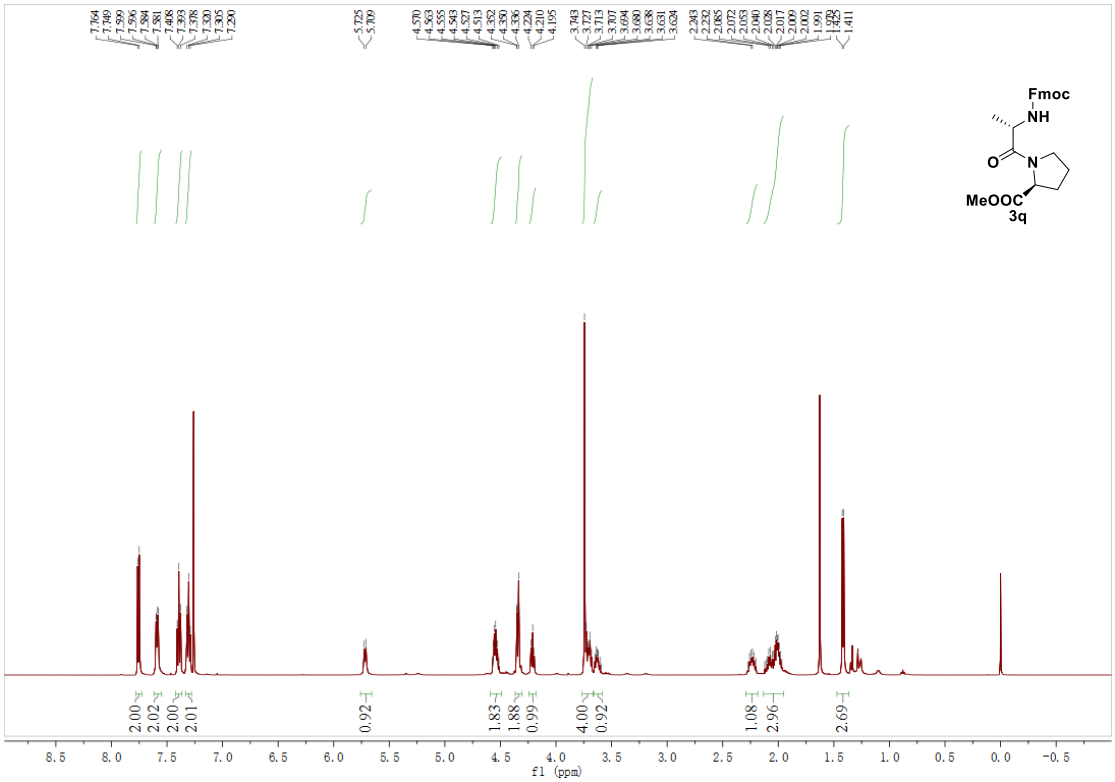
125 MHz, $CDCl_3$, ^{13}C NMR



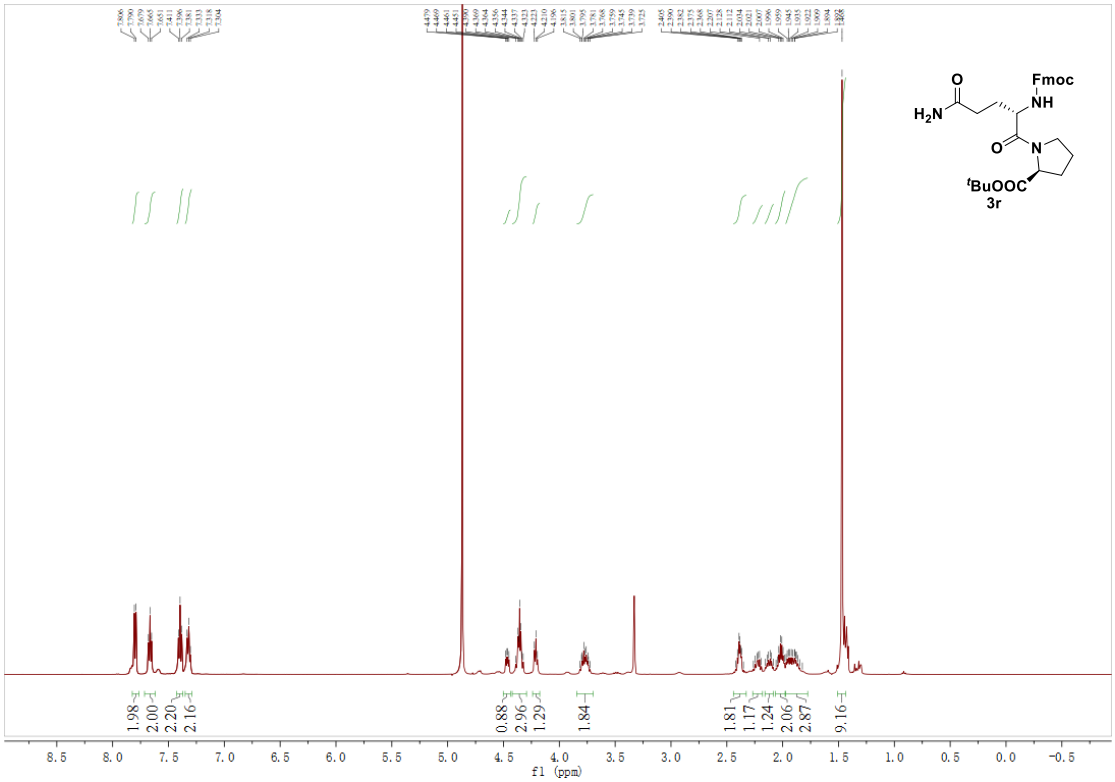
500 MHz, $CDCl_3$, ^1H NMR



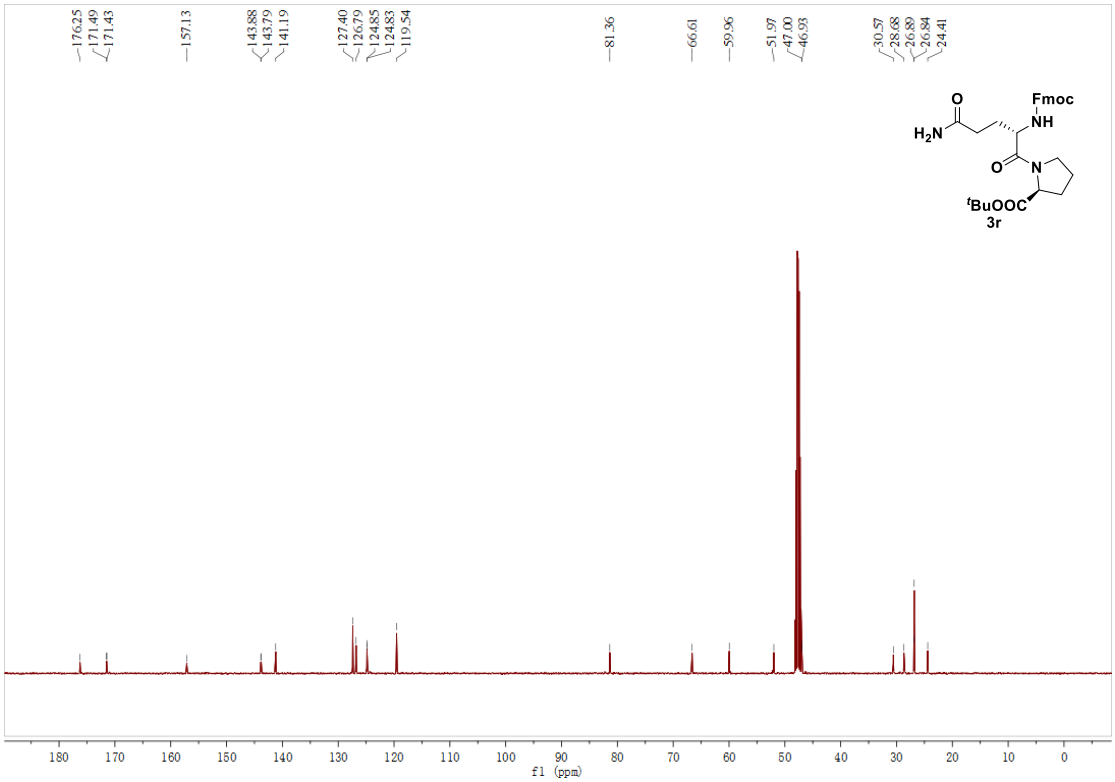
500 MHz, $CDCl_3$, ^1H NMR



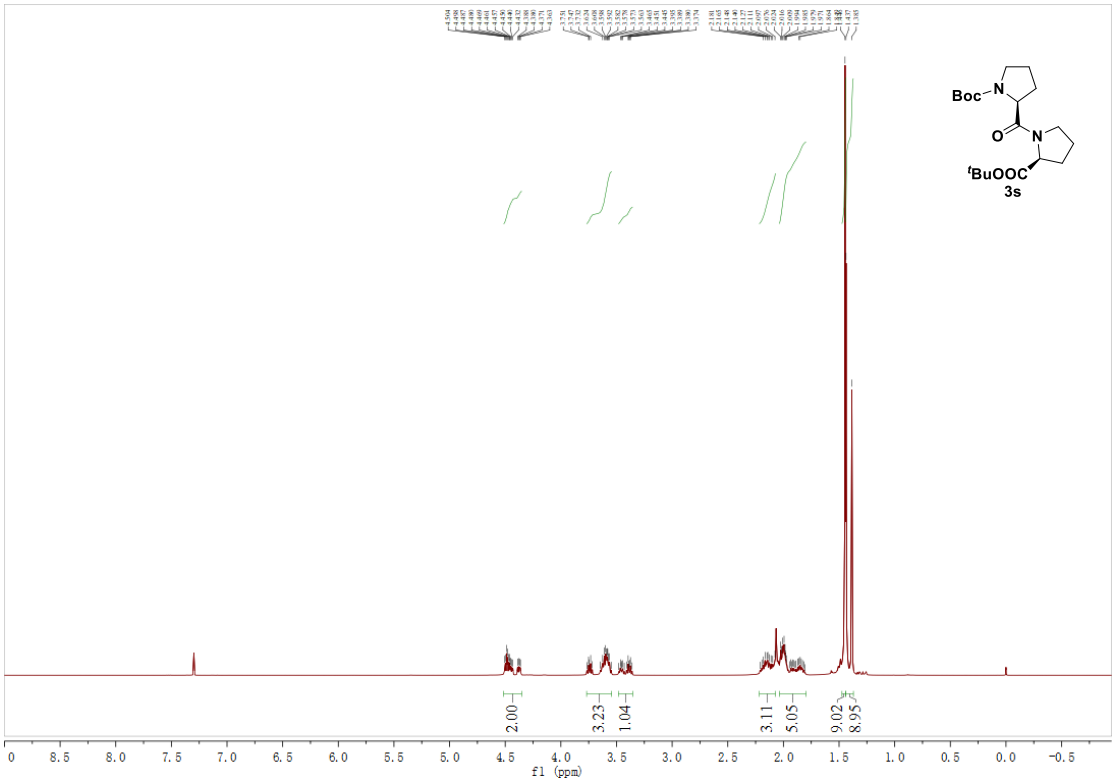
500 MHz, CD_3OD, ^1H NMR



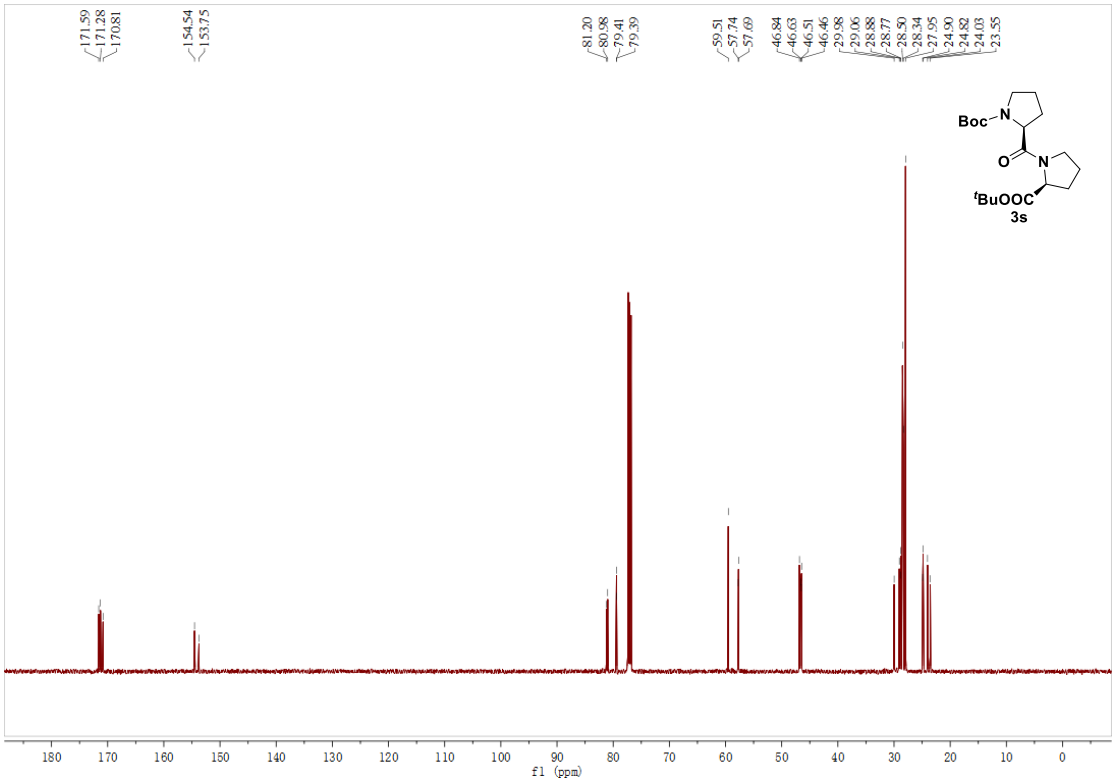
125 MHz, CD_3OD, ^{13}C NMR



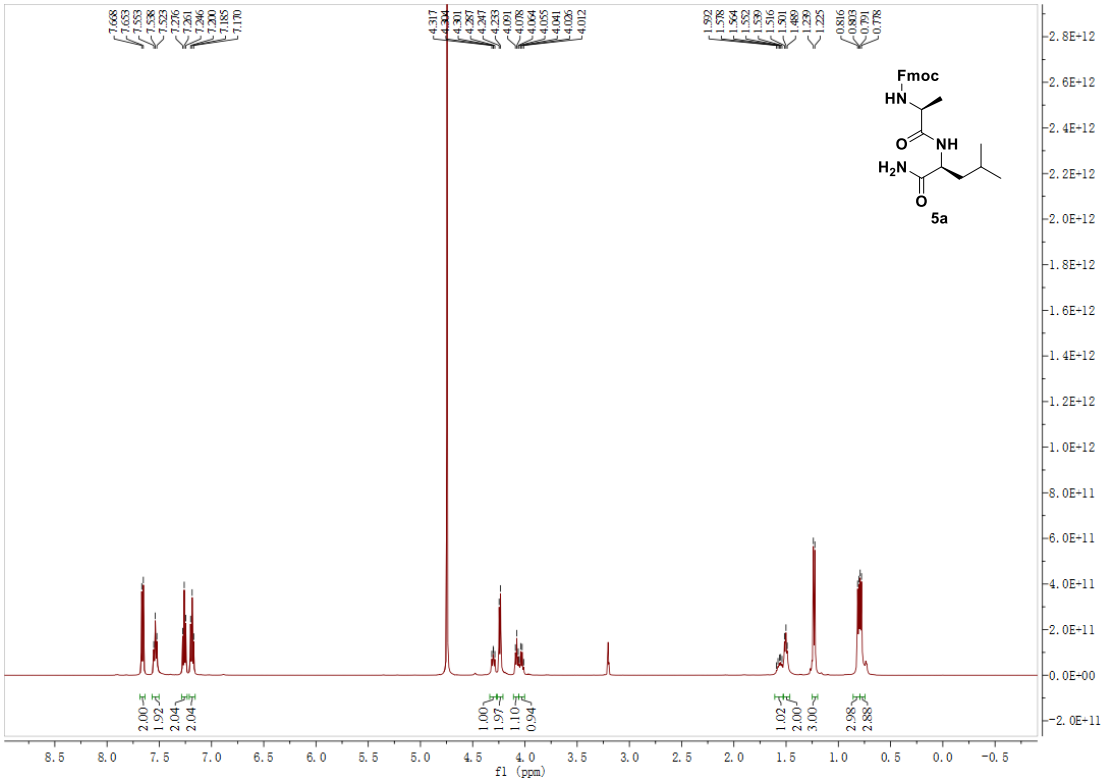
500 MHz, $CDCl_3$, ^1H NMR



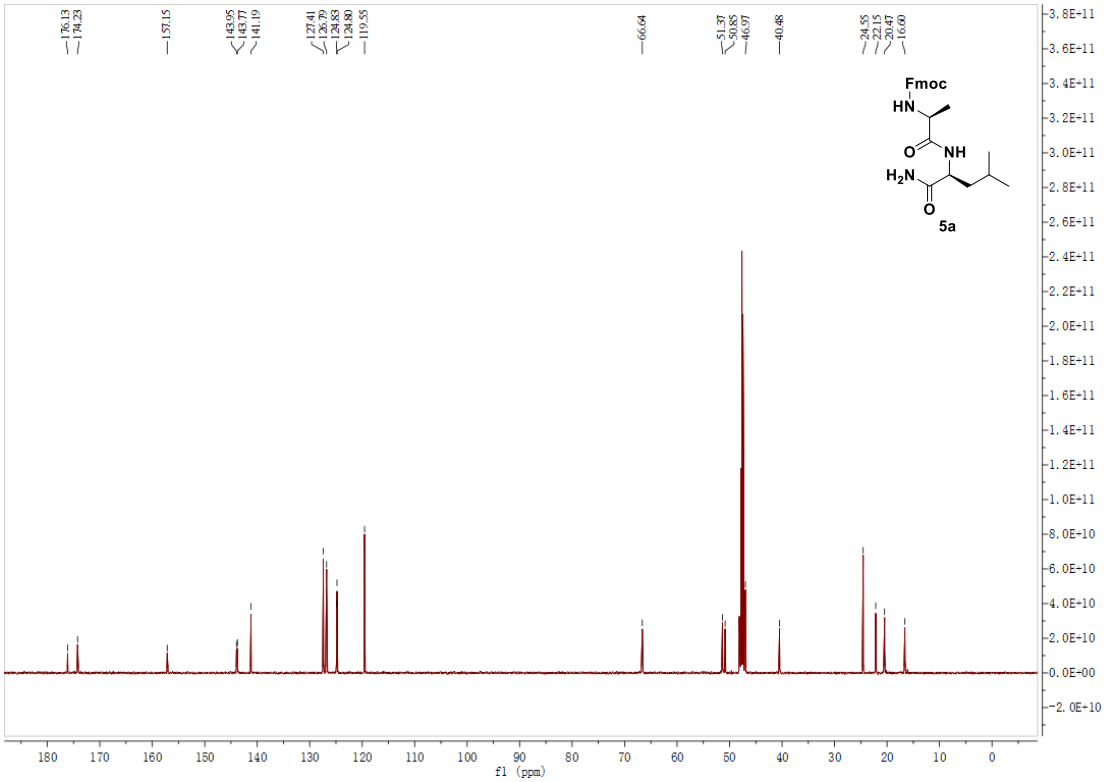
125 MHz, $CDCl_3$, ^{13}C NMR



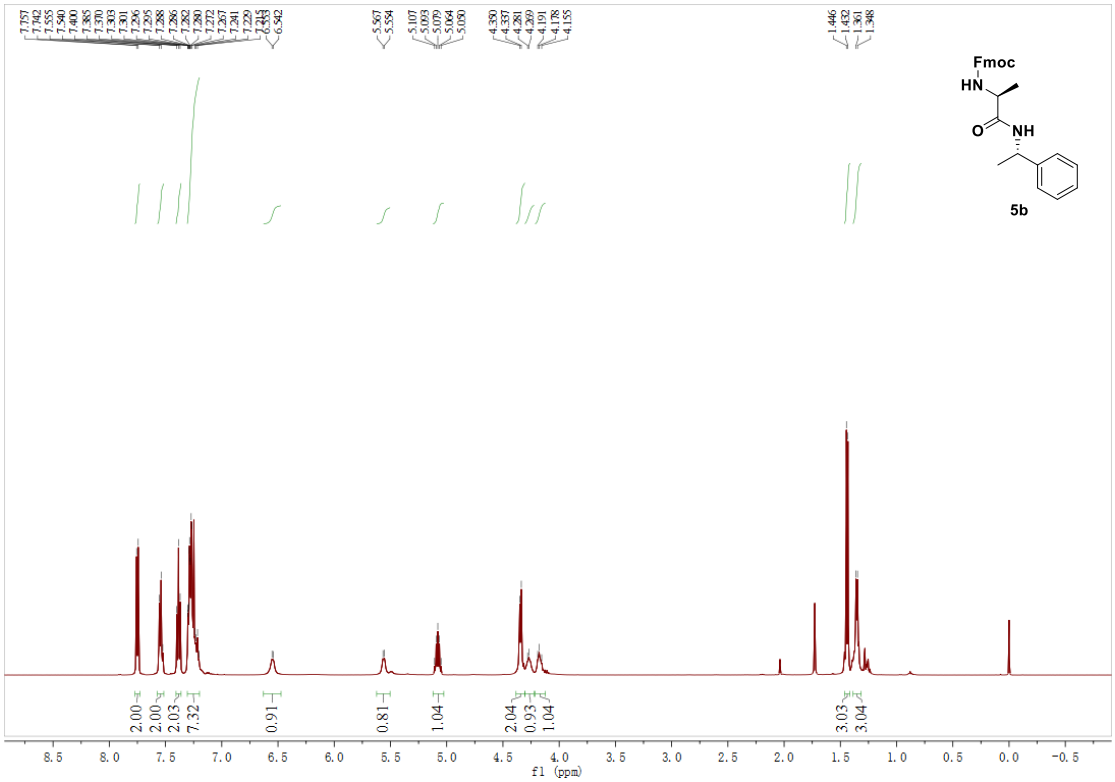
500 MHz, CD_3OD, ^1H NMR



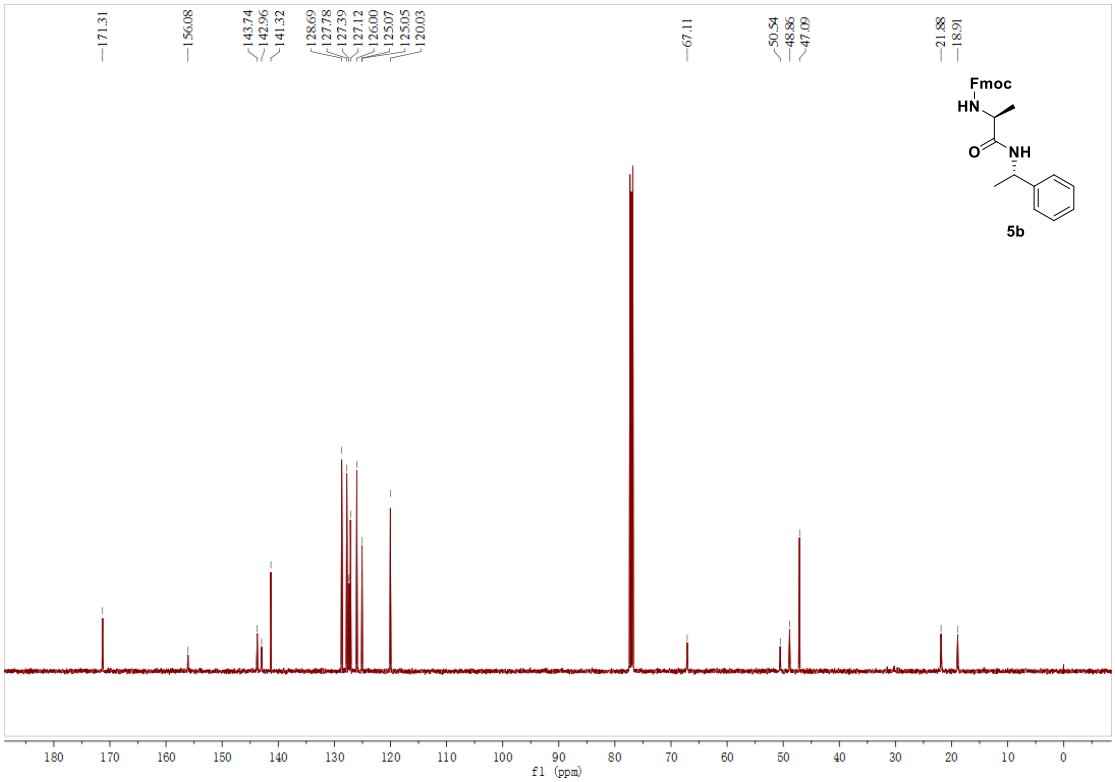
125 MHz, CD_3OD, ^{13}C NMR



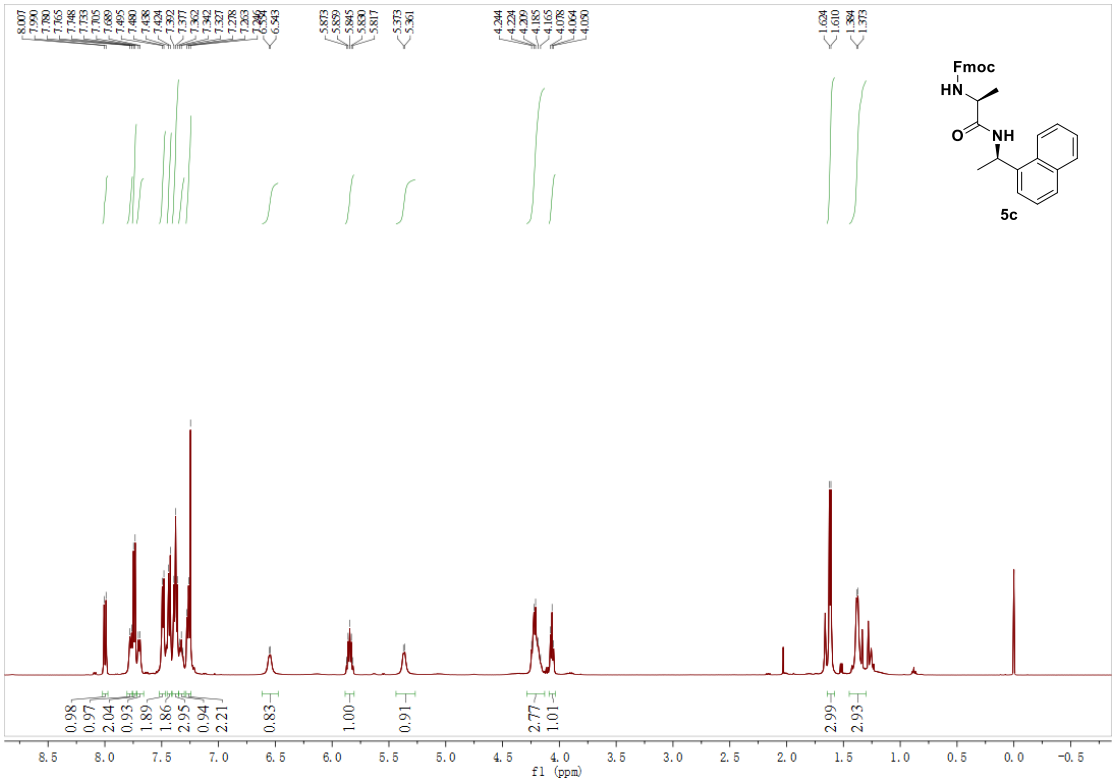
500 MHz, $CDCl_3$, ^1H NMR



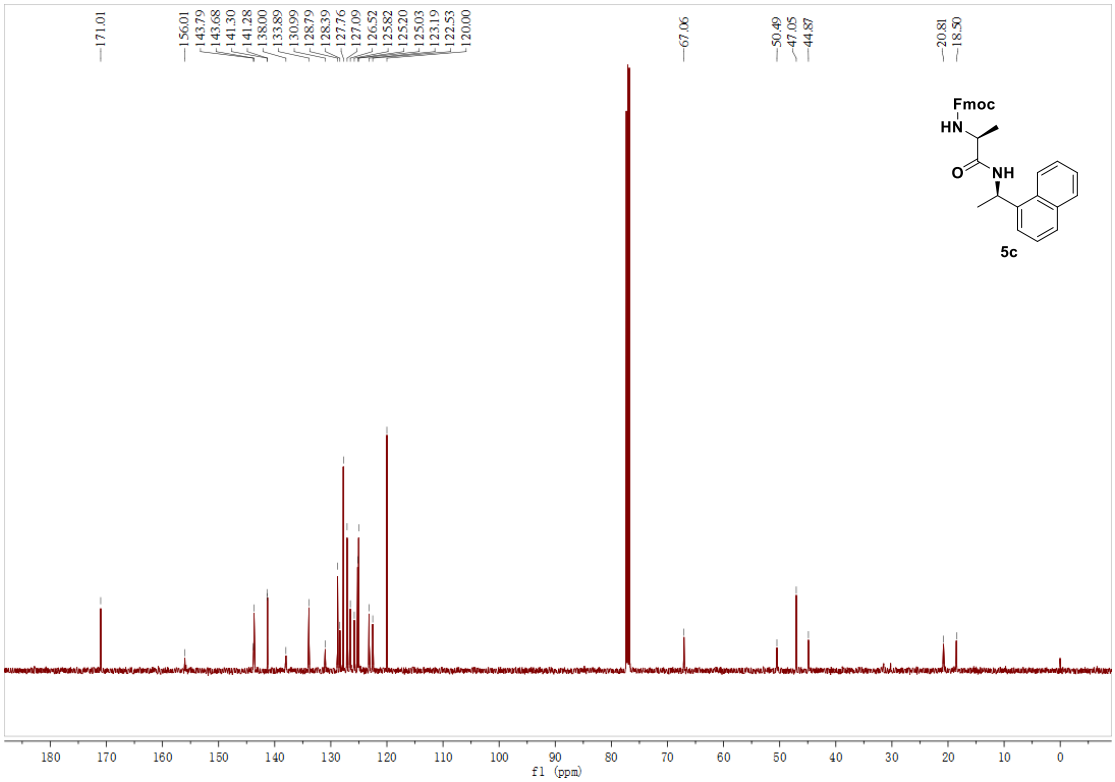
125 MHz, $CDCl_3$, ^{13}C NMR



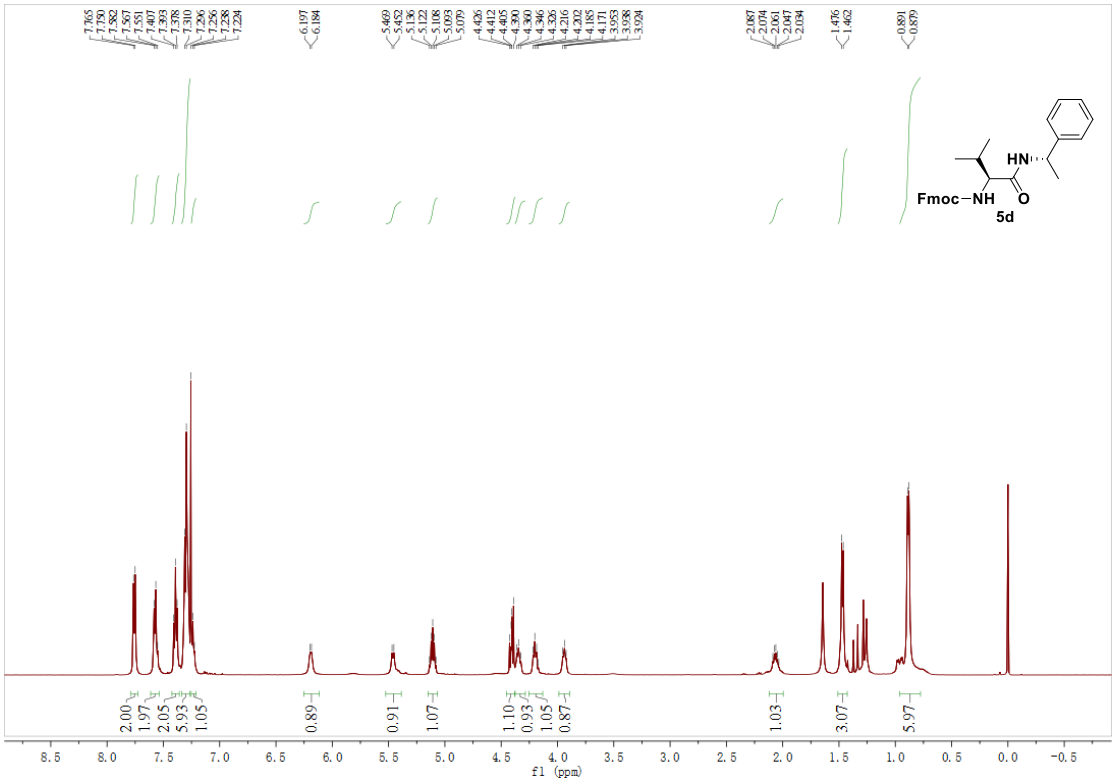
500 MHz, $CDCl_3$, ^1H NMR



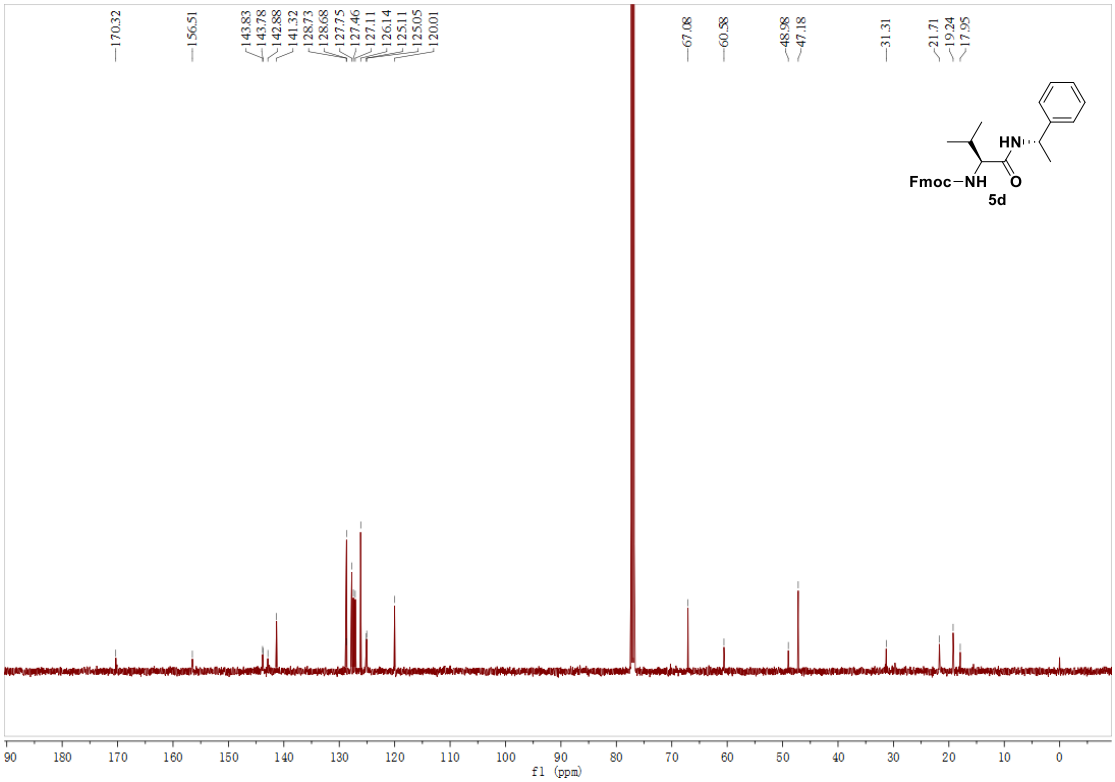
125 MHz, $CDCl_3$, ^{13}C NMR



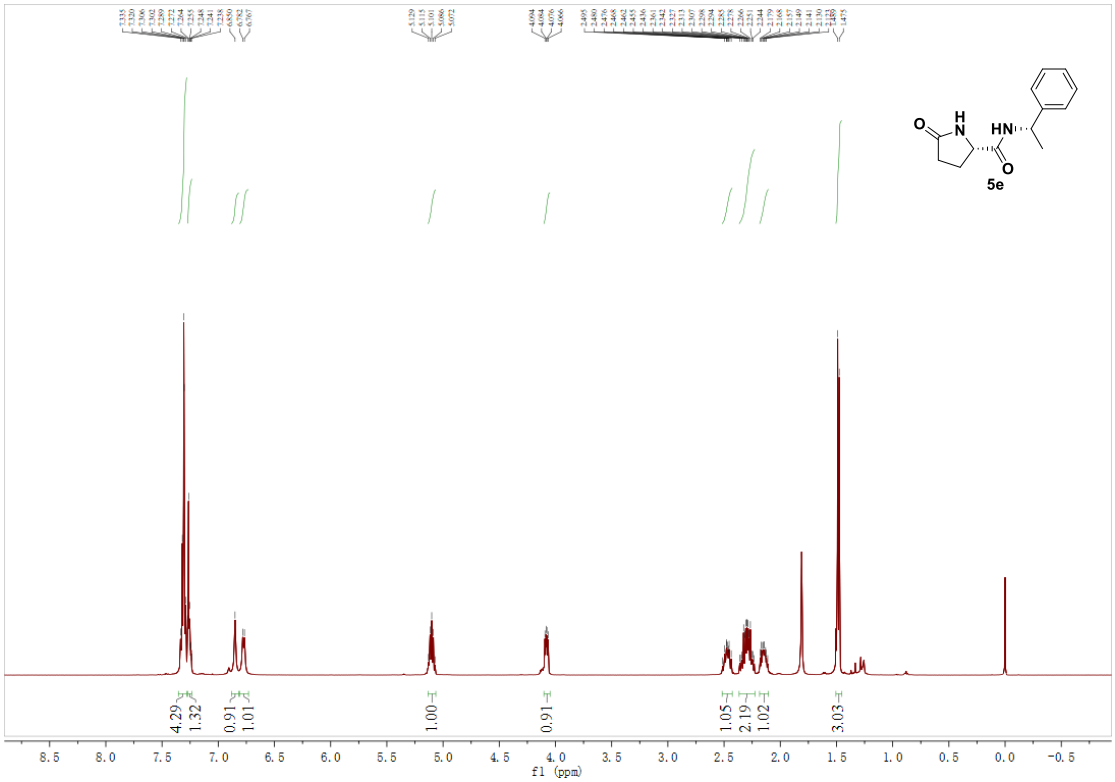
500 MHz, $CDCl_3$, ^1H NMR



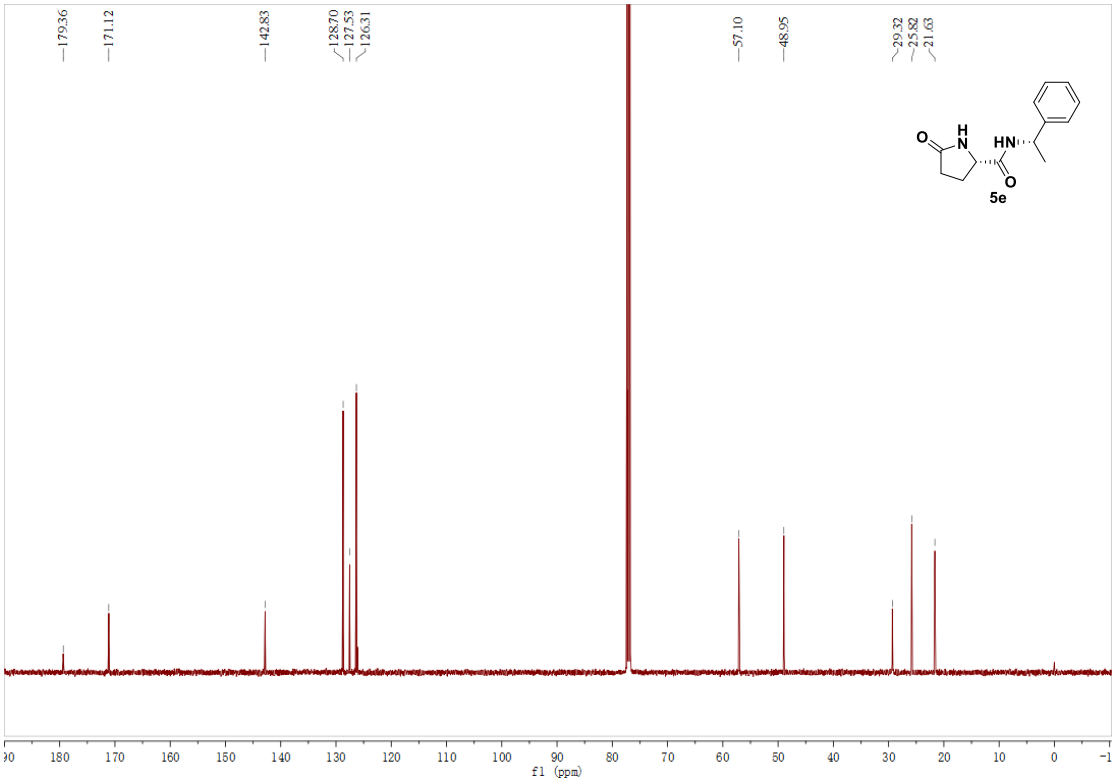
125 MHz, $CDCl_3$, ^{13}C NMR



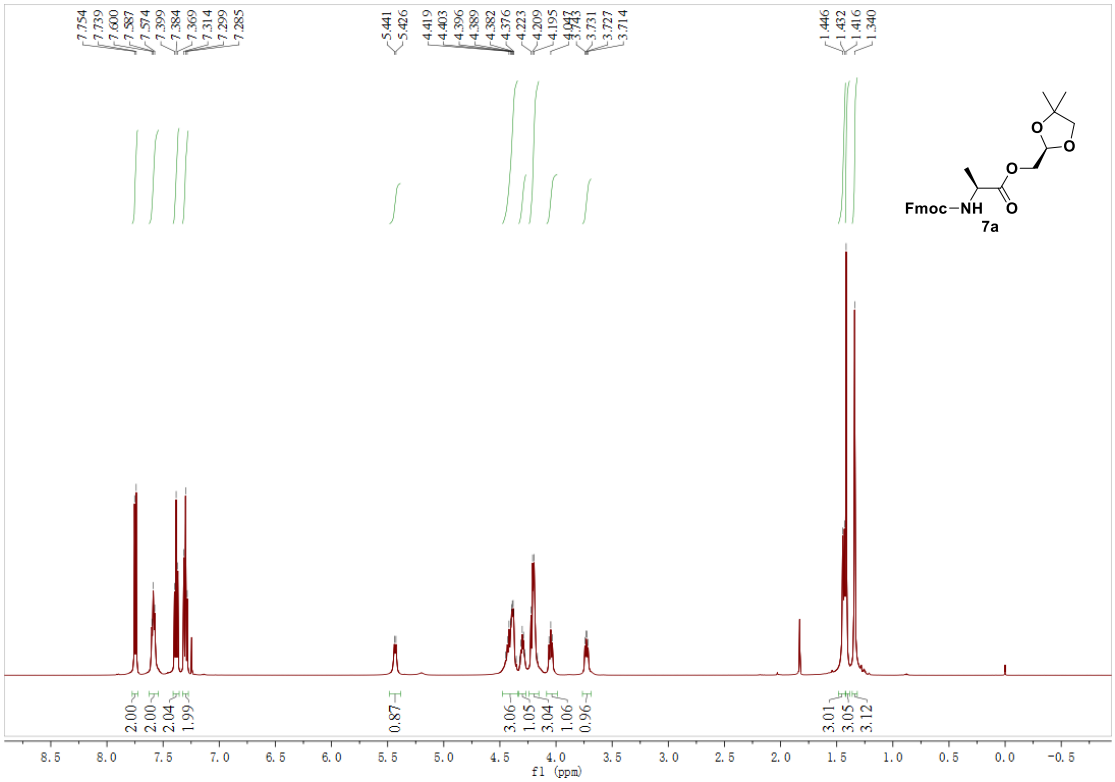
500 MHz, $CDCl_3$, ^1H NMR



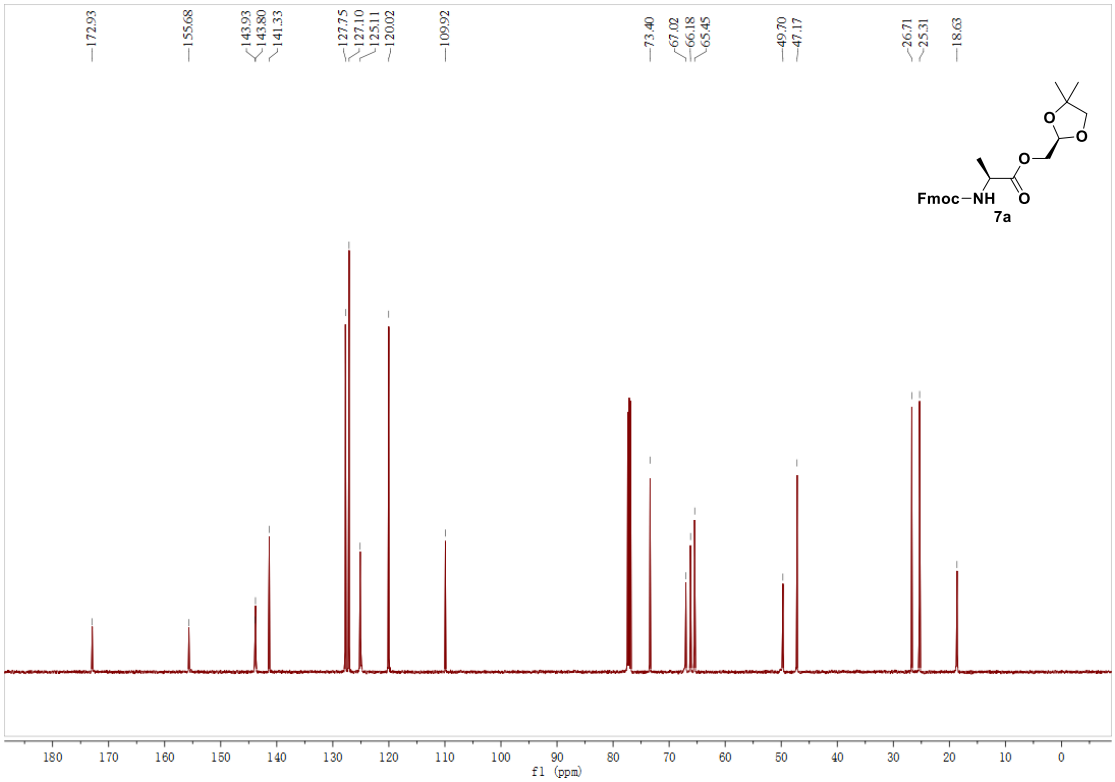
125 MHz, $CDCl_3$, ^{13}C NMR



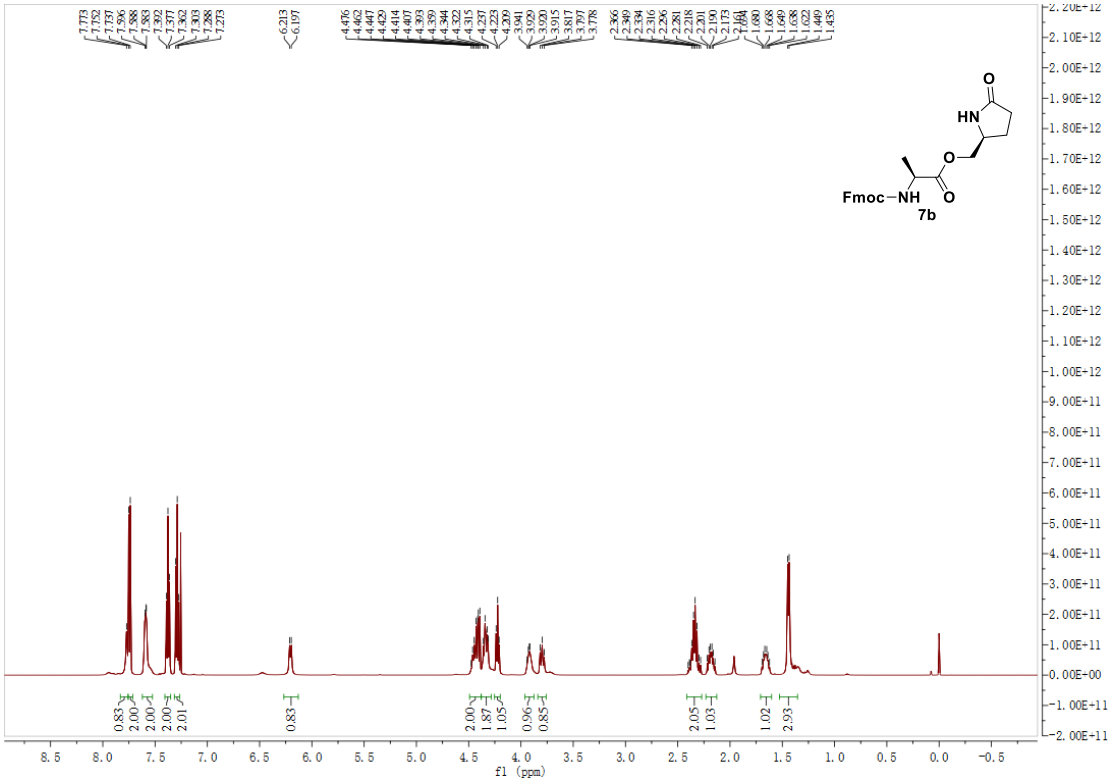
500 MHz, $CDCl_3$, ^1H NMR



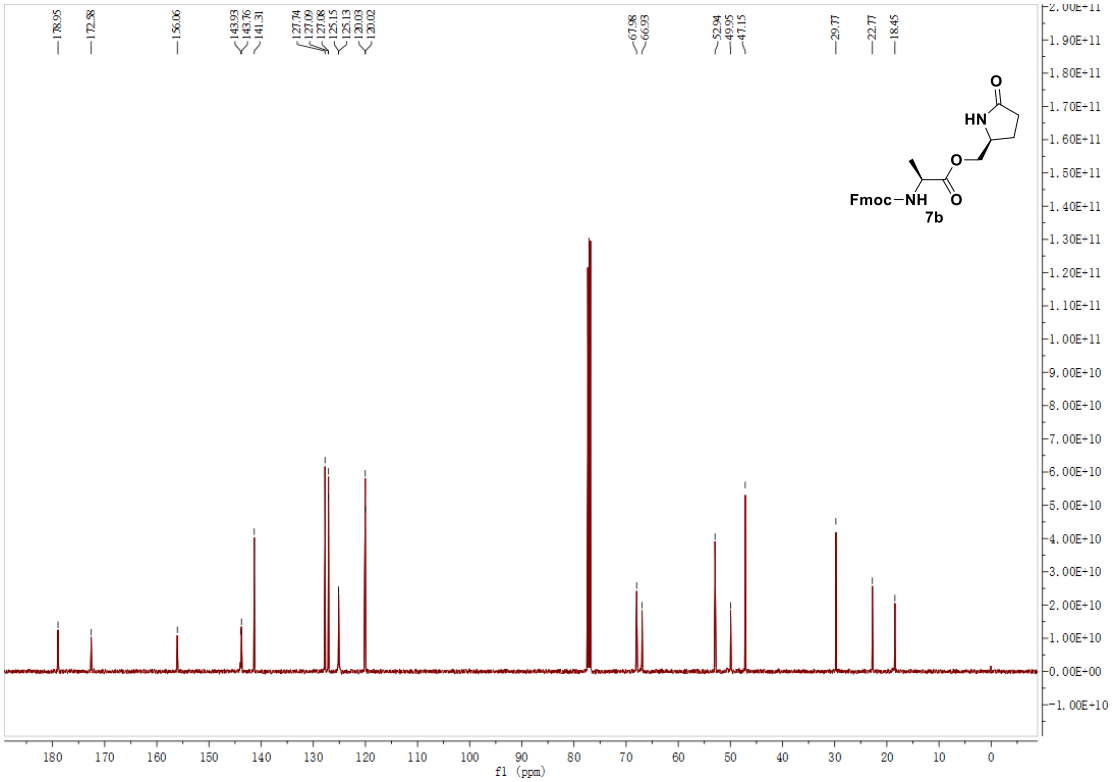
125 MHz, $CDCl_3$, ^{13}C NMR



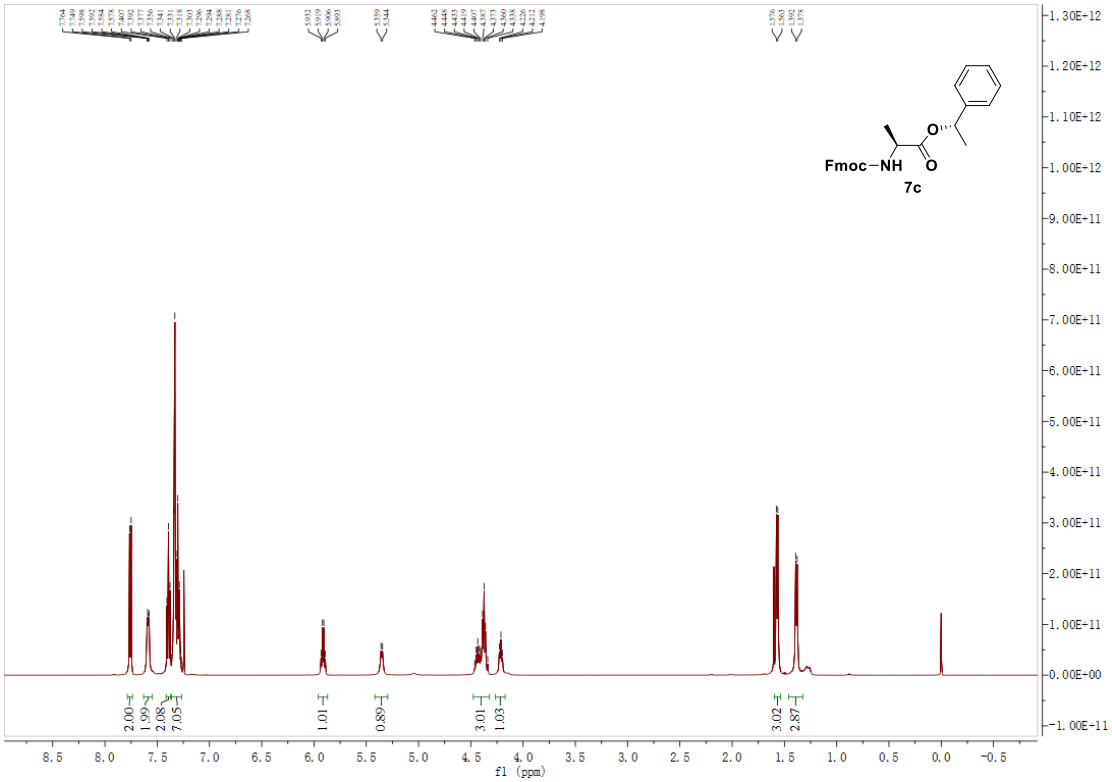
500 MHz, $CDCl_3$, ^1H NMR



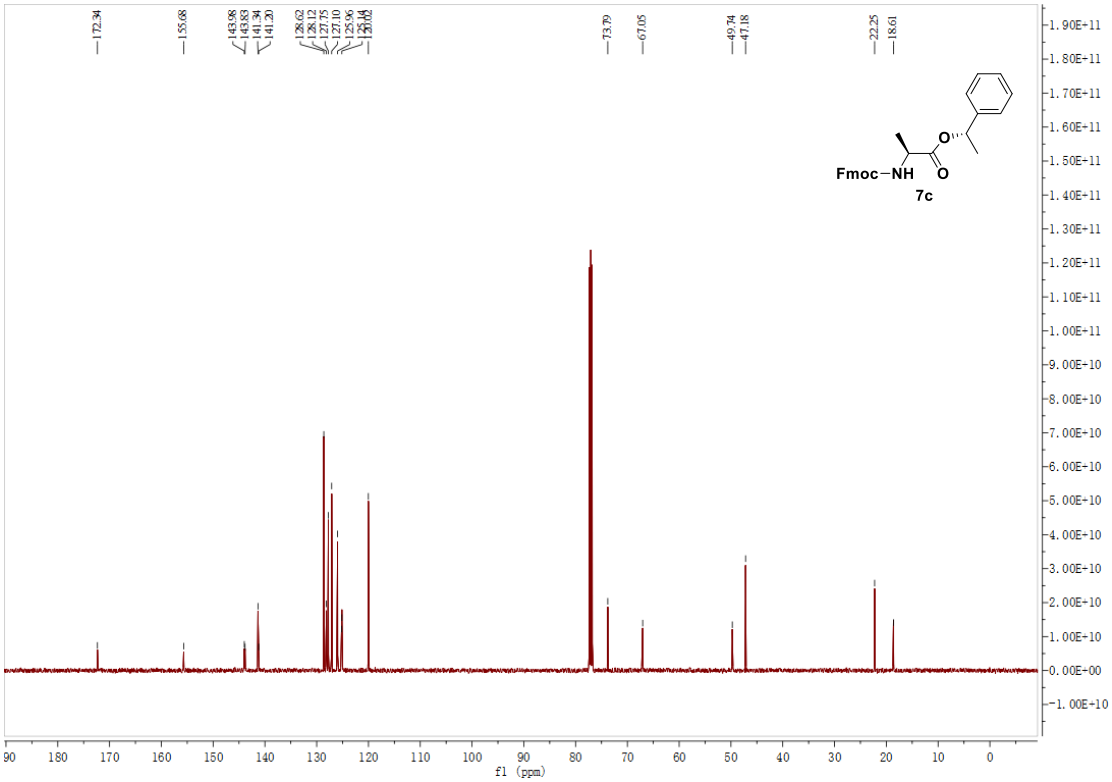
125 MHz, $CDCl_3$, ^{13}C NMR



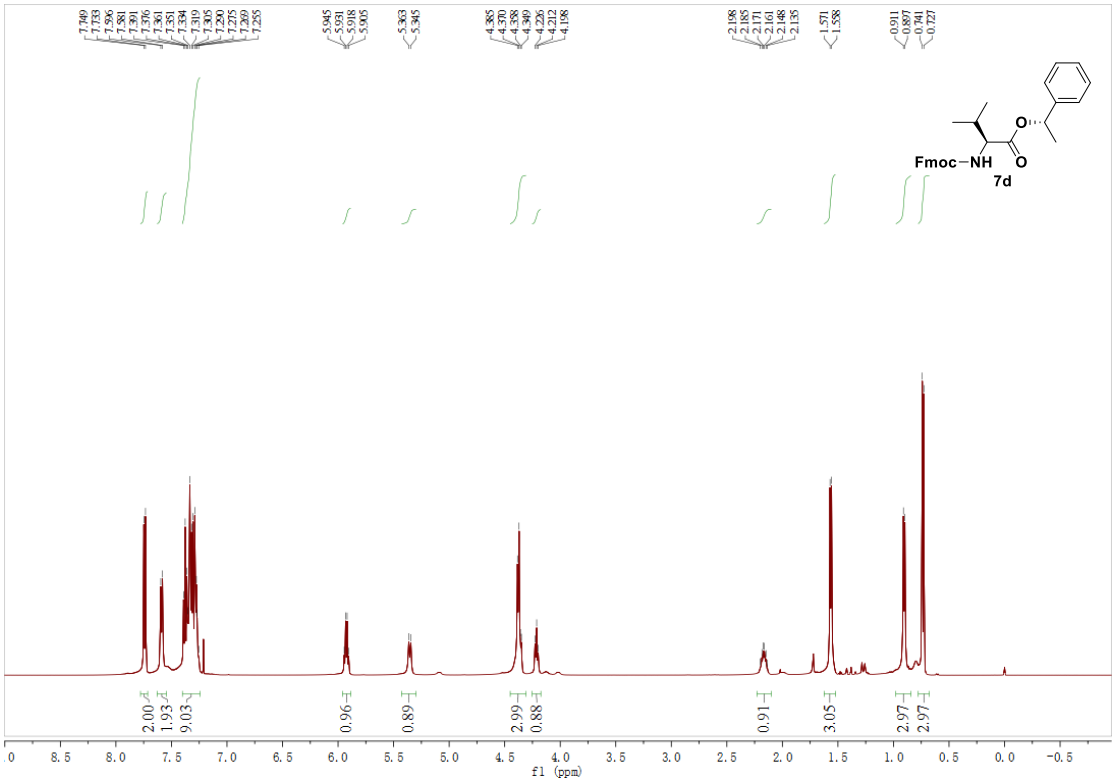
500 MHz, $CDCl_3$, ^1H NMR



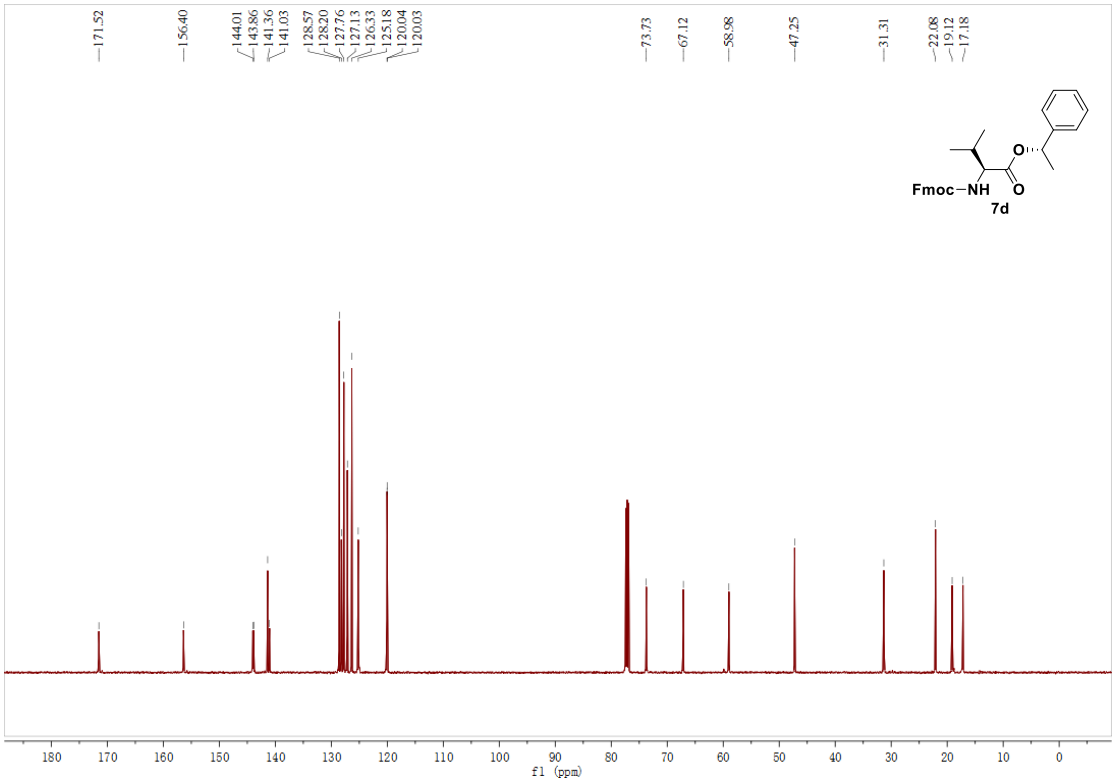
125 MHz, $CDCl_3$, ^{13}C NMR



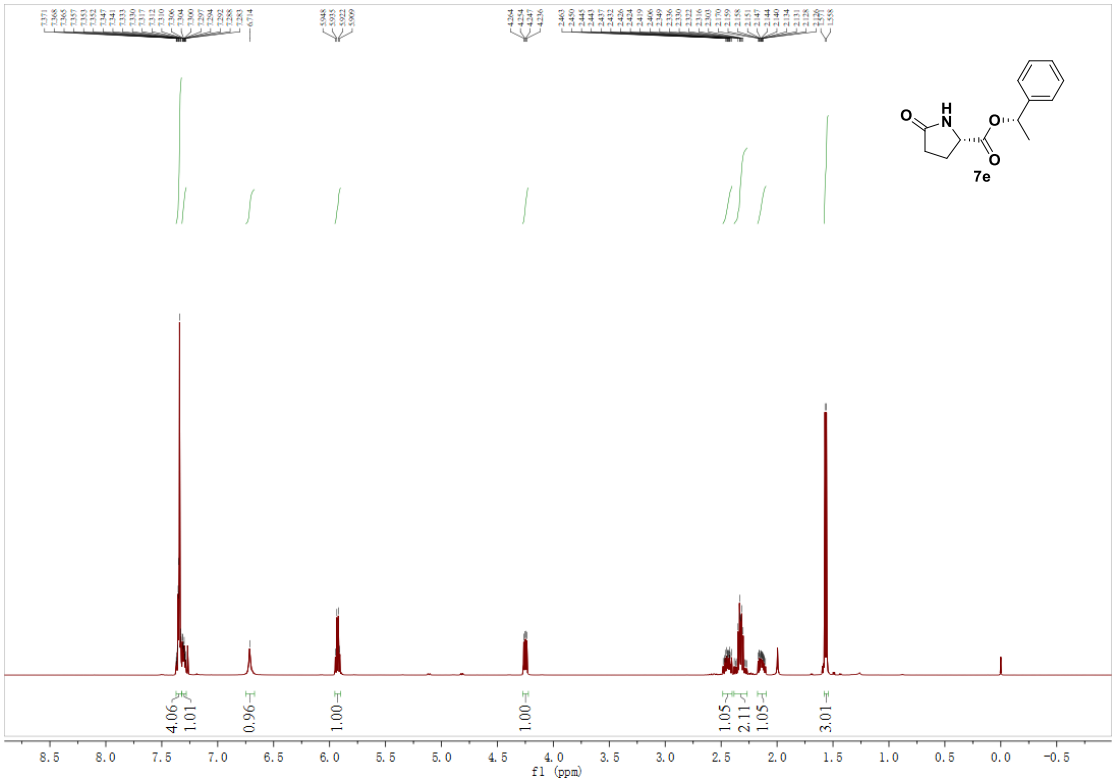
500 MHz, $CDCl_3$, ^1H NMR



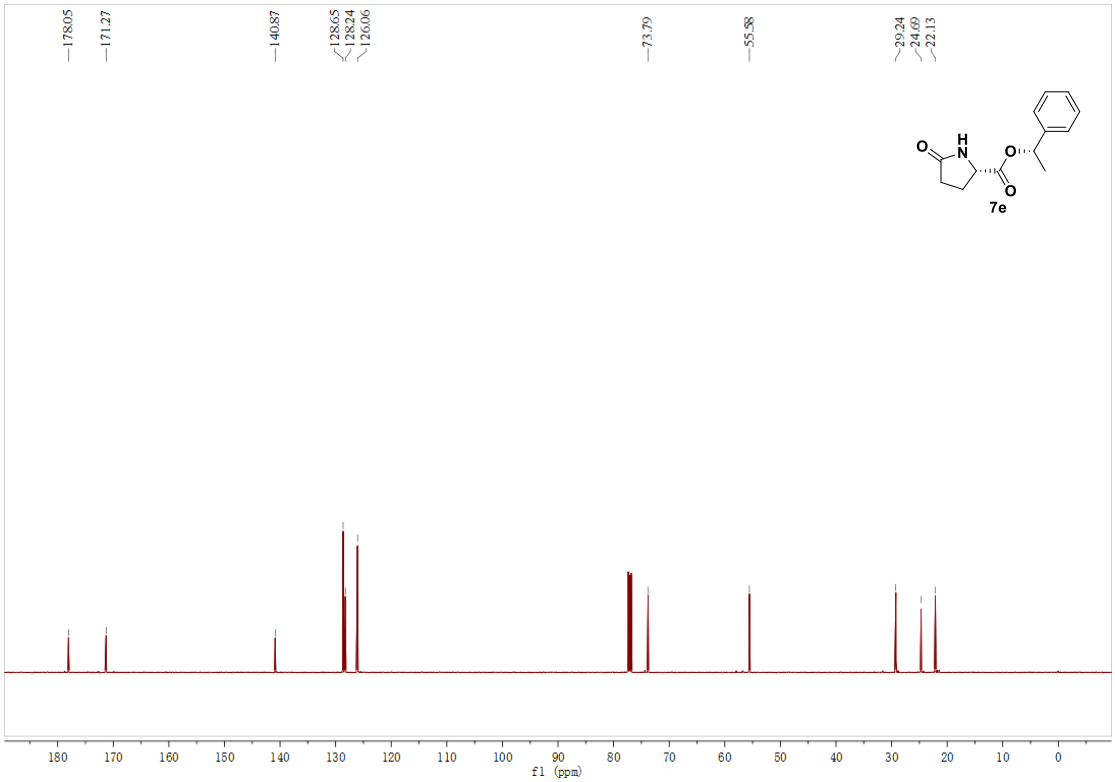
125 MHz, $CDCl_3$, ^{13}C NMR



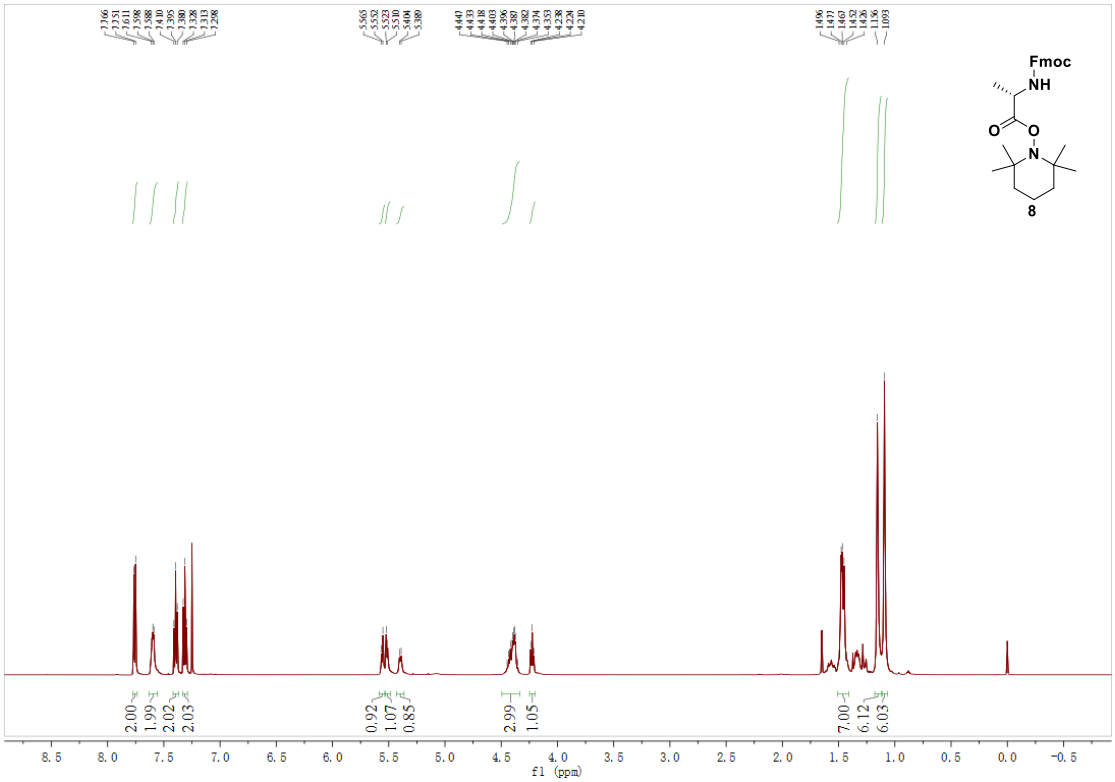
500 MHz, $CDCl_3$, ^1H NMR



125 MHz, $CDCl_3$, ^{13}C NMR



500 MHz, $CDCl_3$, ^1H NMR



125 MHz, $CDCl_3$, ^{13}C NMR